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THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

VOLUME CIII.—1911.

122077
11-5-12

LONDON:
PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.
AND SOLD BY ALL BOOKSELLERS.

MDCCCCXI.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,

16, NEWCASTLE STREET, FARRINGDON STREET,

E.C.

THE CHEMICAL NEWS.

VOLUME CIII.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

No. 2667.—JANUARY 6, 1911.

THE USE OF METALLIC POTASSIUM IN DETERMINING HALOGENS IN BENZOYL DERIVATIVES.

By C. H. MARYOTT.

A METHOD for the estimation of halogens in organic compounds by reduction with sodium and alcohol was described a few years ago by Stephanoff (*Ber.*, 1906, xxxix., 4056). The writer recently attempted to use this method in determining chlorbenzol, but the results obtained were very irregular and unsatisfactory. Before enough sodium had been added to effect complete reduction, the liquid became pasty owing to the separation of sodium ethylate, and this localised and greatly hindered the action of the sodium. By increasing the amount of alcohol above that recommended by Stephanoff, the sodium ethylate could be kept in solution, but the large volume of liquid retarded the reduction, and thus increased both the time and the amount of sodium required. In all cases the results of the analyses were low.

A failure to obtain satisfactory results with Stephanoff's method has likewise been reported by Bacon (*Journ. Am. Chem. Soc.*, 1909, xxxi., 49), who, however, devised a modification of the method, in which accurate results were obtained by heating the mixture for an hour after the solution of the sodium, thus utilising the action of the sodium ethylate upon the halogens. Bacon's method was not tried by the writer, as the article cited came to his attention after the completion of the experiments described below. The long time required, about two hours, would seem to be a disadvantage, and the fact that certain of the benzoyl halogen derivatives, such as monochlor- and monobrombenzol, are attacked, but little, if at all, by boiling with sodium ethylate, a possible source of error in the method.

(NOTE.—The writer boiled monochlor- and monobrombenzol in a concentrated solution of sodium ethylate for three hours, but failed to get any test for halogens upon acidifying and adding silver nitrate. Bacon states in his article that he was unable to convert monobrombenzol into phenetol by heating with sodium ethylate, although 25 per cent of the chlorine was removed from hexachlorbenzol by the same treatment).

The use of potassium instead of sodium as a means of obtaining a more rapid reduction was suggested to the writer by Prof. R. G. Van Name, and upon trial proved to be a great improvement. As the action of potassium upon alcohol is very energetic, a mixture of one volume of 98 per cent alcohol with two of thiophene-free benzol was employed. The presence of thiophene had to be avoided to prevent the formation of potassium sulphide, which would interfere in the subsequent estimation of the halogen. The reduction was carried out in an Erlenmeyer flask, and very little heating was required, so that a plain glass tube about 50 cc. in length, without water cooling, served as a condenser.

The test analyses given below were carried out as follows:—The substance was weighed out in the Erlenmeyer flask, 10 to 15 cc. of the alcohol-benzol mixture added, and the potassium, in small pieces, gradually dropped in through the tube. The weight of potassium required was about ten times that called for by the equation $C_6H_5Cl + 2K + C_2H_5OH = C_6H_6 + KCl + C_2H_5OK$. (Stephanoff's method calls for twenty-five times the theoretical amount of sodium).

A small amount of potassium ethylate usually separated out during the action of the metal, but seemed to have no bad effect upon the reduction. After the action had become less vigorous, about 2 cc. of alcohol were added, the flask carefully heated, and gently shaken from time to time until the potassium was all dissolved. The contents were then shaken with water, the water layer acidified with nitric acid, and the halogen precipitated and weighed as the silver salt. The use of Volhard's volumetric method in estimating the halogens, as done by Stephanoff and Bacon, would, of course, have been feasible, though somewhat less accurate. The time required for an analysis, exclusive of weighings, was about twenty-five minutes. A series of analyses gave the accompanying results.

With the exception of No. 8 the agreement is satisfactory. The low result here is doubtless due to the use of an insufficient amount of potassium, as only six times that required by theory was added. The chlorbenzol was twice re-distilled and that portion distilling between 131·5° and 131·7° used in the analyses.

The results are very concordant but slightly high, probably due to impurity in the brombenzol, as the sample used was a commercial product once re-distilled.

The material used was Kahlbaum's product once recrystallised from hot benzol.

To test the relative efficiency of sodium and potassium in their capacity as reducing agents, an analysis of chlorbenzol was carried out exactly as above described except that sodium (ten times the theoretical amount) was used in place of potassium. Only 84 per cent of the total chlorine was found.

It is therefore evident that potassium is very much more effective as a reducer than sodium, and is consequently better adapted for use upon such substances as the halogen substituted benzols, which belong to the most difficultly reducible class of organic halogen compounds. In the experience of the writer it gives, under the conditions out-

	Weight taken (g.)	Per cent of Chlorine found	Per cent error.
	Chlorbenzol, 31·52 per cent Chlorine.		
1.	0·4436	31·62	+0·1
2.	0·3533	31·46	−0·06
3.	0·4181	31·51	0·01
4.	0·3278	31·44	−0·08
5.	0·4057	31·48	−0·04
6.	0·4245	31·53	+0·01
7.	0·3824	31·52	—
8.	0·3530	30·39	−1·13
	Brombenzol, 50·92 per cent Bromine.		
		Bromine found.	
1.	0·3076	51·29	+0·37
2.	0·3021	51·31	+0·39
3.	0·3028	51·31	+0·39
	Hexachlorbenzol, 74·71 per cent Chlorine.		
		Chlorine found.	
1.	0·1301	75·39	+0·68
2.	0·1199	75·15	+0·44
	p Chloraniline, 27·81 per cent Chlorine.		
1.	0·3081	27·93	+0·12
2.	0·3456	28·00	+0·19

lined above, a complete reduction with the minimum expenditure of time and trouble.—*American Journal of Science*, December, 1910. xxx., p. 378.

FRICTION IN THE BOMB CALORIMETER.

By H. A. ROESLER.

THE heating effect due to the friction of the stirrer in the bomb calorimeter is generally supposed to be very small, but in connection with some calculations relative to the rate of radiation in the calorimeter certain discrepancies were found which could only be explained by the addition of considerable heat from the friction of the stirring apparatus, and a method for determining this heating effect was therefore evolved.

The object of this article is to show how the heat of friction, its magnitude under different conditions, and its relation to the calculation of the radiation correction may be accurately determined.

The rise in temperature during the initial period is due to the algebraic sum of the heat absorbed or evolved by radiation and the heat added by the stirring apparatus.

Let S = rate of rise in temperature due to radiation plus friction.
V = rate of rise in temperature due to radiation alone.
F = rate of rise in temperature due to friction.
M = temperature of the calorimeter.
M′ = temperature of the surrounding medium.
t = difference between the temperature of the calorimeter and that of the surrounding medium.
r = rate of rise in temperature per degree difference in temperature (t) due to radiation.

This value of r may be termed the radiation constant of the calorimeter. It is obtained by dividing the rate of rise in temperature by the difference in temperature of the calorimeter and the surrounding medium.

Then $V = rt$.

$$F = S - V = S - rt.$$

$$t = M' - M.$$

Two values of S, S_1, and S_2 are now determined at temperature differences t_1 and t_2. Then we have—

$$\frac{S_1 - S_2}{t_1 - t_2} = \frac{(V_1 + F) - (V_2 + F)}{t_1 - t_2} = \frac{V_1 - V_2}{t_1 - t_2}.$$

But since—

$$\frac{V_1}{t_1} = r \text{ and } \frac{V_2}{t_2} = r,$$

then—

$$\frac{V_1}{t_1} - \frac{V_2}{t_2} = r.$$

Therefore—

$$F = S_1 - rt_1 = S_1 - \left(\frac{S_1 - S_2}{t_1 - t_2}\right) t_1.$$

The value of F is most accurately determined when one value of t is nearly zero and the other is several degrees above or below, or when one is positive and the other negative.

A number of sets of determinations for S and t, one of which is shown below for the purpose of illustration, were made on the calorimeter used in the Laboratory of the Consolidated Coal Co., Inc. The values for S were obtained by taking ten consecutive readings at intervals of one minute and averaging. The temperature of the calorimeter was then raised about 0·5° by means of a small iron-wire coil, immersed directly in the water and heated electrically, and S was again determined in the same manner. In order to keep conditions as nearly uniform as possible, the calorimeter is surrounded by a water jacket, a double lid placed over the top, and a felt covering one inch thick fitted over all. The stirrer is of the propeller type, the shaft, to which is attached the pulley, projecting out from the top of the calorimeter. The results are given in Table I.

TABLE I.

Ref. No.	Average M′.	Average M.	t.	Average S.
1.	23·013	18·544°	4·469°	0·0128°
2.	22·987	19·065	3·922	0·0112
3.	22·966	19·576	3·390	0·0099
4.	22·947	20·061	2·866	0·0089
5.	22·933	20·556	2·377	0·0079
6.	22·928	21·046	1·822	0·0067
7.	22·939	21·504	1·435	0·0055
8.	22·943	21·987	0·956	0·0047
9.	22·964	22·525	0·439	0·0036
10.	22·980	22·796	0·184	0·0029
11.	22·981	22·825	0·156	0·0029
12.	22·996	23·007	−0·011	0·0024
13.	23·006	23·026	−0·020	0·0023
14.	23·016	23·049	−0·033	0·0023

TABLE II.

Reference No.	F.
1 and 14	0·0024°
1 ,, 13	0·0023
1 ,, 12	0·0024
1 ,, 11	0·0025
1 ,, 10	0·0025
1 ,, 9	0·0026
2 ,, 14	0·0024
2 ,, 13	0·0023
2 ,, 12	0·0024
2 ,, 11	0·0026
2 ,, 10	0·0025
2 ,, 9	0·0026
3 ,, 14	0·0024
3 ,, 13	0·0023
3 ,, 12	0·0024
3 ,, 11	0·0026
3 ,, 10	0·0025
3 ,, 9	0·0027
4 ,, 14	0·0024
4 ,, 13	0·0023
4 ,, 12	0·0024
4 ,, 11	0·0026
4 ,, 10	0·0025
4 ,, 9	0·0026
Average	0·0025

Table III.

Laboratory No.		Av. M'.	Av. M.	*t*.	S.	F.
26627	Initial period	20·940°	19·319°	+1·621°	+0·0065°	
	Final period	20·950	22·017	−1·067	—	0·0026°
26628	Initial period	21·070	19 577	+1·493	+0·0067	
	Final period	21·115	22·282	−1·167	—	0·0029
26629	Initial period	21·625	19 865	+1·760	+0·0075	
	Final period	21·655	22·557	−0·902	+0 0002	0·0027
26630	Initial period	21·805	19 655	+2·150	+0·0080	
	Final period	21·830	22·344	−0·514	+0 0012	0·0026
26631	Initial period . ..	20·270	19 620	+0·650	+0·0042	
	Final period	20·320	22·236	−1·916	−0·0022	0·0026

Taking various combinations of S and *t* and calculating F, we get the results shown in Table II.

Thus F is found to be constant for almost any combination of S and *t*, provided the values for *t* are several degrees apart.

When F is calculated from the readings taken in an ordinary calorific determination the same result is obtained (see Table III.).

The water equivalent of the calorimeter from which these data were taken is 2944 grms., therefore the friction was adding to the apparatus 2944 × 0·0024 = 7·1 calories per minute. During the whole combustion period of six minutes this would be 6 × 7·1 = 42·6 calories.

The value for F obtained on another calorimeter which was equipped with the Mahler stirrer was 0·005°. This instrument has a water equivalent of 2767 grms., which gives 13·8 calories per minute for friction or 82·8 calories for the whole combustion period.

This is much larger than would be suspected, but it is taken into account in the correction for radiation, as shown below. It emphasises, however, the necessity of having an absolutely uniform rate of stirring. The author found upon one occasion that even the loosening of the belt reduced the friction almost 50 per cent.

The best motor to employ is an alternating current induction fan motor. A direct current motor is not so desirable because changes in the voltage will also vary the speed. Stirring by hand should not be attempted if it is possible to obtain a motor, because experience has shown that it is impossible to stir continuously for twenty minutes and maintain a constant speed.

The relation of the friction to the correction for radiation may be shown as follows :—

The formula used for the calculation of the radiation correction is that of Regnault-Pfaunder—

$$C = nV + \frac{V' - V}{\theta' - \theta}\left(\frac{\theta_0 + \theta_n}{2} + \sum_1^{n-1}\theta - n\theta\right),$$

where n = number of minutes in the combustion period.

V = rate of rise in temperature during the initial period.

V' = rate of rise in temperature during the final period.

θ = mean temperature of the calorimeter during the initial period.

θ' = mean temperature of the calorimeter during the final period.

$\theta_1, \theta_2 \ldots \theta_n$ = temperature at the end of the first, second . . . nth, minutes of the combustion period.

θ_0 = temperature at the moment of ignition.

In practice we do not get the values V and V', but V + F and V' + F. If, then, these values be substituted in the formula in the place of V and V' we find that the value of C has been increased to that of C + nF. That is, we get the identical result which would be obtained if we used the true values of V and V' and then added to the value of C thus obtained the correction for the rise in temperature, nF, caused by the friction during the combustion period.

The magnitude of F does not, therefore, affect the accuracy of a calorific determination provided it is uniform throughout the whole time of the determination.—*American Chemical Journal*, xliv., No. 1.

A RAPID METHOD FOR THE IDENTIFICATION OF GAS OILS.*

By F. E. PARK and L. E. WORTHING.

The following data have been gathered in an attempt to develope a means of distinguishing between gas oils derived from different fields. While it is manifestly impossible for an ordinary laboratory to attempt to separate and determine the constitution of the numerous hydrocarbons of gas oils, a simple method of determining the type of oil at hand would often be useful.

From several standpoints a method of identification of gas oils seems desirable. A great deal of the data on water-gas oil results is conflicting. This may possibly be due to a difference in composition of the oil used, a difference which could not be determined by ordinary tests. Some slight attempts have been made to determine the gas making properties of various gas oils by small scale experiments, but the most reliable information on the values of gas oils for gas making purposes is likely to be obtained from their actual use in water-gas practice. Data collected from actual practice require positive and simple methods of identification of the oil in use or a method adapted to the average gas works laboratory. Such a method would aid in the interpretation of results collected from various sources, tend to explain discrepancies, and render results reported in gallons per 1000 more intelligible.

Moreover, the most apparent application of a method of this kind is as an additional check on oil shipments. When water-gas results fall off unexpectedly, it becomes important to discover if there has been a change in the quality of the gas oils. Specific gravity tests and fractionations do not throw a great deal of light on the subject, but further tests are usually dispensed with, as they are expensive, tedious, and liable to be unsatisfactory. Luckily, to prove a change in the oil, it is not necessary to determine its constitution; any simple test serving to identify the oil is sufficient. It is proposed to use the bromine absorption number, which may be readily determined, for this purpose. Before proceeding to describe the process of bromination, it may be well to review briefly the chemical composition of petroleum.

Nature of Petroleum.

In defining petroleum, Mabery states :—"Now, after years of hard labour, I have reached the conclusion that petroleum from whatever source is one and the same substance, capable of simple definition—a mixture in varying proportions of a few series of hydrocarbons, the product from any one field differing from any other field only in the proportion of these series and number of the series."

* Read at the Fourth Annual Meeting of the American Gas Institute From the *Chemical Engineer*, xi., No. 4.

Eight series of hydrocarbons, to each of which a generalised formula may be assigned, are found in petroleum, ranging from the paraffins to the naphthalines :—

1. C_nH_{2n+2} .. .. Paraffins.
2. C_nH_{2n} .. .. Olefines and polymethylenes.
3. C_nH_{2n-2} .. .. Acetylenes.
4. C_nH_{2n-4} .. .. Asphaltic hydrocarbons.
5. C_nH_{2n-6} .. .. Benzenes.
6. C_nH_{2n-8} .. .. Phenylethenes.
7. C_nH_{2n-10} .. .. Phenylethines.
8. C_nH_{2n-12} .. .. Naphthalines.

These expressions, of which only the first five are important, are of use simply as a general classification of oils. Each one represents a group or series—homologous, isomeric or polymeric. In addition to the hydrocarbons, there are present, of course, a variety of related compounds containing oxygen, sulphur, and nitrogen. Such compounds, however, occur in small volumes as compared with the hydrocarbons.

The first formula, C_nH_{2n+2}, represents the paraffin hydrocarbons, of which the first member is methane, CH_4, and which ranges at least as high as $C_{35}H_{72}$. The paraffins are the most important of the open chain or aliphatic series. They are the principal constituents of Pennsylvania petroleum, and have been found in all petroleum except California (Mabery and Hudson, *Am. Chem. Journ.*, April, 1901, p. 255). Each member differs from the preceding one by CH_2. As the number of carbon atoms increases, the number of isomers (compounds having the same percentage composition but differing in the atomic arrangement) increases rapidly. The liquid members follow :—

Name.	Chemical formula	Melting-point (°C.).	Boiling-point (°C.).
Pentane	C_5H_{12}	—	37
Hexane	C_6H_{14}	—	69
Heptane	C_7H_{16}	—	98
Octane	C_8H_{18}	—	125
Nonane	C_9H_{20}	51	150
Decane	$C_{10}H_{22}$	31	173
Endecane	$C_{11}H_{24}$	- 26	195
Dodecane	$C_{12}H_{26}$	12	214
Tridecane	$C_{13}H_{28}$	—	—
Tetradecane ..	$C_{14}H_{30}$	+ 4	252
Pentadecane ..	$C_{15}H_{32}$		—
Hexadecane ..	$C_{16}H_{34}$	18	—

To this must be added the isomeric forms, which differ slightly in boiling-points and physical properties from the normal compounds.

C_nH_{2n} represents the composition of two important types of oils. First, the olefines or unsaturated open chain compounds; second, the aromatic closed ring compounds, the benzene hexahydrides, naphthenes, or polymethylenes—as they are now usually called. The olefines are not as important a constituent of petroleum as formerly supposed. In fact, they have only been positively identified in Canadian oil (Mabery, *Am. Chem. Journ.*, xxxiii., 251).

The naphthalines or polymethylenes are notably present in Russian petroleum, in which they were first studied. Attention was drawn to them because of the similarity of their properties with the paraffins. They have since been identified as the predominant constituents of California and Texas petroleum, and are present in Ohio Trenton limestone oil. Members of the series from C_7H_{14} to $C_{15}H_{30}$ were isolated from California crude.

The series C_nH_{2n-2} is called the acetylene series after its first member. The lower members, however, are never found in petroleum. Texas oils contain hydrocarbons of series C_nH_{2n-2} from $C_{14}H_{26}$ to $C_{19}H_{36}$. These hydrocarbons are characteristic of oil from Texas, Louisiana, and Ohio. Compounds of this formula are certainly not all true acetylenes. The isomers can be explained by the assumption of two methylene rings connected as in the manner of diphenyl, with a sufficient number of side chains or connected carbon atoms between rings to account for the formula.

In oil from Trenton limestone Mabery and O. H. Palm found hydrocarbons having the composition $C_{19}H_{36}$, $C_{21}H_{46}$, $C_{22}H_{42}$, and $C_{24}H_{46}$ (*Am. Chem. Journ.*, xxxiii., 251). With those compounds were members of the C_nH_{2n} series as high as $C_{17}H_{34}$. Texas oils contain the next series C_nH_{2n-4} from $C_{29}H_{38}$ to $C_{25}H_{46}$. This series also predominates in the heavy asphaltum oils from Louisiana.

There are probably oils of series containing much less carbon in the higher fractions of Louisiana and Texas oils, but decomposition on fractionation prevents separation necessary in order to study the pure compounds. The most promising method of getting at the constitution of these heavy hydrocarbons is by fractional filtration through Fuller's earth.

The series C_nH_{2n-6} represents the benzenes or aromatic hydrocarbons. Traces of benzines have been found in nearly all oils, even in Pennsylvania oils. The lighter fractions of California oil, however, contain the largest per cent of hydrocarbons of this series, which includes, of course, the toluols and xylols.

1. Benzine .. .. C_6H_6
2. Toluol .. .. C_7H_8
3. Xylol .. .. C_8H_{10}
4. Cumene .. .. C_9H_{12}
5. Cymene .. .. $C_{10}H_{14}$

Maybery and Hudson (*Chem. Ind.*, 1900, p. 502) in fractionating a California oil found 35 per cent benzine in a fraction boiling near 80° C., in the 109° to 110° C. fraction 70 per cent toluol, 135° to 140° C. fraction 75 per cent xylol, and at 220° to 222° C. the distillate was solid with naphthaline. If there are any paraffins in California oil they occur in distillates below 70° C. (*Am. Chem. Journ.*, xiii., 233).

Members of C_nH_{2n-8} and C_nH_{2n-10} series have also been identified in small amounts in California petroleum. The oil from the mid-continental fields has a wide variation in composition, and contains many different series. Small quantities of oxidised compounds are found in petroleum as acids and phenols. Phenols occur principally in California oils. Nitrogen is found in all oils, and in the case of California oil, compounds of the formula $C_{12}H_{17}N$ to $C_{17}H_{21}N$ constitute from 10 per cent to 20 per cent of the crude petroleum. The nature of the sulphur compounds in petroleum is not well understood. It appears in many forms from occluded H_2S to so-called thiophanes. In Lima oil sulphur appears to be in the form of sulphides. Ten compounds, from C_2H_6S to $C_{12}H_{26}S$, have been isolated (*Am. Chem. Journ.*, xiii., 233). Canadian petroleum in the higher fractions contains compounds of the formula $C_nH_{2n}S$ (*Proc. Am. Acad.*, xli., 89). Texas oil, besides organic sulphur, contains large amounts of free hydrogen sulphide.

Summarising the characteristics of the principal American oils :—Texas oil is remarkable for its asphaltic inert properties. Pennsylvania paraffin oil is even more chemically inert, California oil contains benzines, and Canadian oil contains open chain unsaturated hydrocarbons. The other types have less striking peculiarities. As gas oils usually are fractions of about 33° B., they contain not only a portion of the original oil, but are liable to contain products of decomposition caused by cracking. These decomposition products may cause the oil to exhibit properties—as it does, indeed, contain compounds—completely different from the original.

Process of Bromination.

The notion of treating hydrocarbon oils with bromine has been derived from the custom of identifying vegetable or animal oils by their so-called bromine or iodine numbers.

Table I.—*Fractional Distillation.*

Name.	Specific gravity.	Point of distillation.	Up to 302 F.	302—573° F.	572—602° F.	662° up.	Distillation loss.
Laclede, St. Louis. ..	31·7° B.	196° F.	4·3 p. c.	30·7 p. c.	39·3 p. c.	20·7 p. c.	5·0 p. c.
	Specific gravity		59·2° B.	38·7	30·7	26·2	Carbon
Denver, G. and E. ..	32·4	164	3·3	37·3	41·3	14·3	0·8
Co.	Specific gravity		60·4	35·7	30·3	26·3	Carbon
Florence, Col.	34·0	130	3·7	34·3	45·7	16·0	0·3
	Specific gravity		44·8	36·3	34·0	30·0	Carbon
Sugar Creek, Mo. ..	32·5	173	4·0	37·7	21·7	33·3	4·3
	Specific gravity		53·8	38·0	31·3	27·0	Paraffin
Florence, Col.	30·9	194	1·0	7·7	37·7	53·0	0·6
No. 2	Specific gravity		—	40·9	33·3	29·6	Carbon
Boulder, Col.	32·0	168	0·7	1·7	27·7	66·0	3·9
	Specific gravity		—	—	33·7	32·4	Paraffin
Canada, crude	41·9	174	19·3	43·3	31·7	1·0	4·7
	Specific gravity		57·2	46·1	37·3	—	Pitch

Table II.

Name.	Specific gravity.	Total bromination.	Bromination substitution.	Bromination addition.	Sulphur.	B.T.U.
D.C.G. Co., Utl., 11,831 . ..	34·3	26·67	6·42	13·83	0·26	18,867
San Antonio, Tex.	22·1	10·38	3·57	3·24	2·09	18,750
Los Angeles, Cal.	20·1	22·22	9·81	2·60	0·80	18,538
Pennsylvania	34·4	11·20	2·99	5·22	0·26	18,843
Laclede, St. Louis	31·7	24·98	5·45	14·04	0·56	19,526
Denver G. and E.C...	32·3	10·70	2·58	5·54	0·52	18,851
Florence, Col.	34·0	5·48	1·48	2·52	0·31	20,131
Sugar Creek, Mo.	32·4	16·41	4·46	7·49	0·25	19,311
Florence, Col., No. 2	30·9	14·15	3·37	7·41	0·35	18,904
Boulder, Col.	32·0	7·98	2·40	3·18	0·28	—
Canada, crude	41·8	4·87	0·46	3·95	0·50	—
Pentane	—	0	0	0	0	—
Toluol	—	2·80	1·40	0	0	—
Benzol	—	0	0	0	0	—
Xylol	—	6·34	2·43	1·48	0	—

Name.	Specific gravity.	Point of distillation.	Up to 310° F.	310—475°.	475—570°.	570—690°.	690° up.	Distillation loss.
Utl. 11,831, D.C. Gas Co. ..	34·4	211	7·3	29·3	21·3	32·7	8·3	1·1
Spec. grav.	—	—	53·7	40·5	33·5	28·5	26·5	Carbon
San Antonio, Tex.	22·1	172	3·3	13·0 (1·7 water)	22·7	53·0	4·2	2·1
Spec. grav.	—	—	51·3	35·1	27·8	23·9	Asphalt	Carbon 10 per cent
Los Angeles, Cal.	20·1	218	5·7	15·3	12·0	33·7	21·3	Asphalt 2 per cent loss
Spec. grav.	—	—	54·3	39·6	29·3	24·1	22·1	Carbon

The idea of determining the amount of bromine an oil will take up is not a recent one, but dates back to 1857, to Cailletet, a Frenchman, who describes a method of treating oil with an alcoholic solution of bromine, and titrating the excess bromine with a turpentine solution until the colour is discharged.

In 1881, A. H. Allen proposed a method for brominating oil in which the bromine was liberated in contact with the oil by the decomposition of a water solution of sodium hypobromite with hydrochloric acid. Two years later Mills and Snodgrass proposed the use of carbon bisulphide as a solvent. These various schemes were all intended, principally at least, for the identification of vegetable or animal oils, which gave characteristic bromine absorptions, and for the detection of their adulteration.

The most satisfactory method involves the use of carbon tetrachloride as a solvent. This scheme was first used by McIlhenny (*Journ. Am. Chem. Soc.*, xvi., 275; ii., 1084), and is recommended principally because of the increased stability of the carbon tetrachloride bromine solution, and of a sharper end-point in titrating. One of the reasons for the increased stability of the carbon tetrachloride over the carbon bisulphide can be inferred from a consideration of their boiling-points,

Carbon bisulphide boils at 43° C.; bromine at 63° C.; carbon tetrachloride at 77° C.

Another is the fact that carbon bisulphide forms various sulphur bromides in solution, and liberates free hydrobromic acid.

The method we have used is an adaptation of McIlhenny's. Twenty-five cc. of a tenth normal solution of bromine in carbon tetrachloride, previously standardised against sodium thiosulphate, is agitated with ¼ to ½ grm. of the oil to be tested in a stoppered Erlenmeyer flask. Before mixing, the sample of oil should be dissolved in 25 to 30 cc. of carbon tetrachloride. The mixture is then allowed to stand in the dark for thirty minutes. The carbon tetrachloride solution and the oil to be tested should be previously dried by use of a few sticks of fused calcium chloride.

At the end of thirty minutes about 100 cc. of distilled water is added to the flask, with 2 grms. of potassium iodide, and the unabsorbed bromine titrated against a tenth normal sodium thiosulphate water solution. Starch solution is used as an indicator. The end-point is reached when the bromine colour of the oily layer has disappeared, and the iodine blue of the starch and water solution is just discharged. The oily carbon tetrachloride solution should

appeared before titrating or insufficient bromine solution has been used.

The hydrobromic acid formed during the bromination is titrated against sodium thiosulphate by adding half a grm. of sodium iodate to the flask, after the titration is finished, and titrating to the second disappearance of the blue colour. Or the hydrobromic acid may be titrated against N/100 caustic after separating from the oily layer. Better results can be obtained from the iodate method by first separating the oily layer from the water solution.

Both the absence of sunlight and the careful drying of both oil and tetrachloride are most necessary, as light accelerates the bromination of the saturated compounds, giving rise to an undue proportion of substituted bromine; and the presence of the smallest amount of moisture is even more effective in accomplishing the same result. The addition of the bromine solution and subsequent titration with sodium thiosulphate need not, however, be made under artificial light, as by carefully duplicating the conditions of experiment very concordant results may be obtained. The total bromination number is the number of grms. of bromine absorbed per 100 grms. of oil. The bromine substitution number is the amount of bromine found as hydrobromic acid after the bromination is completed, calculated to the same basis. The bromine addition number is calculated by subtracting twice the bromine substitution number from the total bromination. This calculation is based on the following equations :—

$$\underset{\text{Ethylene}}{2C_2H_4} + Br_2 \quad \underset{\text{Ethylene bromide.}}{2C_2H_4Br} \quad \text{or} \quad \underset{\text{Ethylene.}}{C_2H_4} + Br_2 = \underset{\text{Ethylene di-bromide.}}{C_2H_4Br_2}$$

Example of substitution :—

$$\underset{\text{Toluol.}}{C_6H_5CH_3} + Br_2 = \underset{\text{Hydrobromic acid.}}{C_6H_5CH_2Br} + HBr$$

It is evident that for every substituted bromine compound formed an equal amount of hydrobromic acid is formed. Hence, it is necessary to deduct both the bromine of substitution and the hydrobromic acid bromine from the total absorption to find the amount going to form addition products. Both the olefines and the acetylenes form addition products, so that in a general way it may be assumed that large addition numbers indicate acetylenes, olefines, or ring compounds with unsaturated side chains. Large substitution numbers benzines and small total bromination—paraffins or naphthenes. If paraffins were attacked by slight exposure to daylight, substitution products would be formed.

While it would not be fair to assume that the members of the different series are present in direct proportion to the substitution, addition, or absence of bromination in the case of a single oil, between the various oils the results of bromination would indicate which oil contained more of a particular series.

The above described process was carried out on samples of oils differing largely in character and from widely separated fields. Through the courtesy of the St. Louis, San Antonio, Los Angeles, and Denver Gas Companies, and the Standard Oil Company, we received samples of gas oils of the principal types found in the United States. We also tested samples of Canadian crude. Fractionations, sulphur content, heat values, and bromine absorption are given in Tables I and II.

Pennsylvania oil, Florence, Col., Boulder, Col., and Texas oil appear to have a predominance of paraffins or naphthalines. Detroit City Gas Company's oil, and Laclede (St. Louis) oil seem to be largely olefines or unsaturated ring compounds, whilst Los Angeles oil is remarkable for the presence of benzines, and Canada oil for the absence of them.

The proportionate large amount of additional bromination in the case of Canadian crude is further evidence of the presence of small amounts of olefines. The apparent presence of olefines or other unsaturated compounds in the Detroit City Gas Company's oil, and in the Laclede, is probably due to the cracking of the original oil. Toluol shows exactly the theoretical substitution, xylol shows a preponderance of substitution, and some additional products probably due to impurities. Both these products, of course, belong to the benzine series.

The lack of action in the case of benzine is to be expected in the absence of carrier. It is readily brominated in the presence of certain foreign bodies which promote the action. The failure of benzine to react with bromine in a pure state indicates what an important effect a mixture of oils and the products of bromination may have on the amount of bromine absorbed. To test the effect of mixing oils on bromine absorption, the Detroit and San Antonio oils were mixed in exactly equal proportions by weight with the following results :—

By test—	
Average total bromine absorbed ..	20·60
Average substitution	5·36
Average addition	9·88
Same by calculation—	
Average total bromine absorbed ..	18·52
Average substitution	5·00
Average addition	8·53
Effect of mixing benzine and Florence oil—	
Average total bromine absorbed ..	4·91
Average substitution	2·12
Average addition	0·68
By calculation—	
Average bromine absorbed	2·74
Average substitution	0·74
Average addition	0·63

It is apparent that the effect of increasing the number of constituents increases the amount of bromination. The total bromination of a mixture may then be assumed to be above figures calculated from bromination numbers of pure constituents. Evidently impurities in oil have the effect of accelerating slightly the bromination of hydrocarbons aside from their own action in absorbing bromine. Hydrogen sulphide is the impurity which probably causes the greatest error in interpreting the results of bromination, as it forms hydrobromic acid and free sulphur. If all the 2·09 per cent of sulphur in San Antonio oil were hydrogen sulphide, the error would be 5·2 grms. of bromine per 100 grms. of oil, or sufficient to account for half the total bromination. However, in oils giving large bromine absorptions the amount of hydrogen sulphide present is nil, or negligible, and the possible error due to its presence is very slight. To test the value of the method in identifying a single type of oil, the following samples were brominated :

Grand Rapids and St. Louis gas oils are included in Table III. only because they are all approximately of the same type. Detroit gas oil has the following average bromination numbers :—

Total bromination	30·13
Addition..	14·73
Substitution	7·70

It varies from the average figure by +9·8 per cent to −10·7 per cent. Such variation would be expected in view of the range in specific gravity from 33·6° B. to 36·1° B. The Denver Gas Co.'s oil shows a striking similarity to the Pennsylvania gas oil, and, in turn, to the San Antonio gas oil, though the first two are undoubtedly largely paraffins, and the last a polymethylene or naphthaline. An idea of the bromine values of oils which are published can be obtained from Table IV.

The report of Mills and Snodgrass on shale oil in Table IV. shows that the absorption of bromine with shale oil varies inversely as the density of the oil.

Summary.

By treating gas oils with bromine dissolved in carbon tetrachloride, under specified conditions, a characteristic bromine absorption number can be obtained having an

Table III.

Kind of oil.	Car. No.	Sp. gr. (°B.).	Total bromination.	Addition.	Substitution.
Sta. A, Utl.	11,831	34·4	26·67	13·83	6·42
Sta. A, Utl.	8,553	36·1	28·18	14·06	7·06
Sta. A, Utl.	7,867	36·0	29·45	14·39	7·53
Sta. A Works, pump	—	36·1	31·35	16 03	7·66
Sta. B, Utl.	8,513	33·6	32·07	15·33	8·31
Sta. B, Utl.	7,545	33·6	33·07	14·54	9·23
Grand Rapids, Utl. .	9,405	33·0	27·18	9·54	8·82
Laclede, St. Louis..	—	31·7	24·98	14·04	5·45

Table IV.

Oil.	Sp. gr. (°B.).	Total bromination.	Addition.	Substitution.	
Shale	35·8	48·2	—	—	(a)
American pet.	36·6	32·3	—	—	(a)
Russian pet.	32·0	1·9	1·70	0·10	(a)
Cal. pet., Puente Field	—	18·8	—	—	(b)
Puente Field	—	18·3	—	—	(b)
Shale	33·5	22·24	—	—	(c)
	31·9	20·59	—	—	(c)
	28·0	12·59	—	—	(c)
	26·0	11·72	—	—	(c)
Mineral..	45·0	27·57	—	—	(c)
Illuminating	45·5	30·31	—	—	(c)

(*a*) Allen, "Commercial Organic Analysis," ii., 95.
(*b*) Mabery, *Am. Chem. Journ.*, April, 1901, p. 255.
(*c*) Mills and Snodgrass. *Journ. Soc. Chem. Ind.*, Nov. 29, 1883, pp. 336, 435.

allowable variation of ± 10 per cent, which may be used to identify the oil and serve as an additional check on the composition of gas oils, besides the specific gravity and fractionation tests. As an aid in distinguishing between saturated and unsaturated hydrocarbons, the amount of hydrobrobromic acid formed during the bromination is determined. The total amount of bromine absorption and the per cent of hydrobromic acid formed are considered together in deciding as to the type of oil. For purposes of water-gas manufacture the method is exceedingly reliable and sufficiently accurate, and, in the case of a single sample, the addition and substitution numbers may, by carefully duplicating the conditions of experiment, be checked to within 1/10 grm. of bromine in every case. The 50 cc. burettes are the only apparatus required. About two hours are necessary for a duplicate determination.

EFFICIENCY IN THE ELECTROLYTIC PRODUCTION OF METALLIC CALCIUM.*

By FRANCIS C. FRARY, HENRY R. BICKNELL, and CARL A. TRONSON.

Most of those who have worked on the electrolytic production of calcium have been content to describe their methods and apparatus, with perhaps an analysis of a selected lump of their product, but say nothing of the current efficiency obtained. Muthmann (*Zeit. Electrochem.*, 1904, x., 508), in the discussion of a paper by Rathenau, states that by using an electrolyte consisting of two parts of calcium chloride to one part of the fluoride, and raising the iron cathode as the metal accumulated, he obtained a "good" yield. Goodwin (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1403), electrolysing pure calcium chloride in a similar way, obtained a current efficiency of 21·5 per cent to 41·9 per cent. Woehler (*Zeit. Elektrochem.*, 1905, xi., 612), using an electrolyte containing 100 parts of the chloride to 17 parts of the fluoride, claims an efficiency of over 80 per cent, but states that the electrolyte deteriorated in time, probably owing to the formation of the hydrated oxychloride, and that hydrogen (!) is then liberated at the cathode, and the yield decreases. He used a current of 40 ampères at 33 to 38 volts, but does not say how often or for how long a time this efficiency could be obtained. Tucker and Whitney (*Journ. Am. Chem. Soc.*, 1906, xxviii., 84) improved the apparatus of Goodwin, and claim an efficiency of 60 per cent, using the pure chloride as electrolyte, but give no data to support the claim. As far as we are able to ascertain, no one else has published any results on the efficiency of the various processes which have been proposed.

During previous work in this this laboratory (Frary and Badger, *loc. cit.*), efficiencies as high as 46 per cent were obtained, but, unfortunately, the only runs in which the necessary data were taken were made under unfavourable conditions. As it was certain that better results could be obtained and had been obtained in some of the runs for which no data were at hand, these were not published at the time, and the work was continued by the present authors.

The apparatus used was the same as that described by Frary and Badger (*loc. cit.*), and consisted essentially of a large crucible of Acheson graphite having a water-cooled bottom and serving as anode, and a water-cooled iron cathode a little over an inch in diameter. The crucible was enclosed in a protective layer of refractory material, and especial pains were taken with the contact between it and the positive cable. The cathode could be raised or lowered at will by means of a screw mechanism.

From preliminary experiments it was decided that the occasional feeding of the fresh electrolyte and irregular raising of the cathode were two important causes of low efficiency. Intermittent addition of electrolyte caused irregularities in the height of the melt and its temperature, especially the latter. Too great cooling of the electrolyte caused the deposition of the metal in a spongy form, in which state it was readily lost. Spongy portions were also formed when the stick of metal extended too far below the surface of the melt, the current density being insufficient to melt the metal at the point of contact with the electrolyte, and thus produce a solid stick. (In most cases a rod of about 1 cm. diameter was obtained, so the cathode area was about 1 to 1½ sq. cm.). This spongy metal was very likely to be dislodged and swept away by the vigorous convection currents which were always present; it also gave trouble by growing toward one side or other of the crucible, causing an increase of current at that point, with consequent increased growth of metal and a higher temperature, until finally the calcium on the edges would melt, and, being connected with the main stick only by thin pieces of metal, would be easily swept away by the electrolyte. When the end of the stick of metal was kept just below the surface of the electrolyte, the spongy metal at first formed melted almost at once, and its surface tension drew it into a compact globule which was almost immediately frozen by the cooling effect of the rest of the stick and the water-cooled cathode. Thus a solid stick was easily obtained. To get the best results it was found necessary for one person to devote all his attention to the raising of the cathode and the addition of the electrolyte, making both operations practically continuous.

The chloride used was some of Merck's C.P. granulated, which had previously been used in desiccators. It was dried in an iron crucible over a four-post Bunsen burner, and preserved in a stoppered bottle.

In starting up a run the cold fused chloride remaining in the crucible from a previous run was heated until dry by directing the flame of a blast-lamp upon it. Then a small portion of it was fused by drawing an arc from the side of

* Paper presented at the Eighteenth General Meeting of the American Electrochemical Society, in Chicago, October 13—15, 1910. The work described in this paper is a continuation of that published by Frary and Badger (*Trans. Am. Electrochem. Soc.*, 1909, xvi., 185), where a summary and discussion of previous work on the electrolytic production of calcium will be found.

the crucible with the aid of a graphite rod. A small current was used until contact was made with the cathode, when more current was put on and the graphite rod removed. As soon as good contact was assured, the direct current was shut off, and an alternating e.m.f. of about 30 volts applied. The current usually rose rapidly to about 200 amperes, being regulated by raising or lowering the cathode, and the upper part of the crucible was soon filled with molten chloride. A sufficient supply of electrolyte was added at this time to fill up the crucible, and when all was ready, the alternating current was thrown off and the direct current thrown on. Readings of the time, voltage, and amperage were taken at once. The voltmeter and ammeter were read every five minutes during the run, and the average of these readings considered to be the average voltage and amperage for the run. The current varied very little during each run, as it was taken from the 110-volt lighting circuit through a constant resistance. There was no trouble with the so-called "anode effect," except when the electrolysis was started before a sufficient amount of the electrolyte had been melted down by the alternating current.

(NOTE.—A sample of the electrolyte was taken at such a time, when the "anode effect" had been more than usually troublesome, and the per cent of silica present determined. Only 0·056 per cent was found, confirming the results obtained in the previous paper, and indicating that current density rather than impurities should be blamed for this "effect").

The formation of the metal under the cathode was watched very carefully, great care being necessary to get a good start. We aimed to withdraw the cathode and metal as rapidly as it was possible to do so without striking an arc. It will be noticed in the table of results that practice in doing this increased the yield obtained. When the electrolysis is going on properly, and the stick of metal is at the right depth, the electrolyte seems to flow rather rapidly across the surface in a fixed direction, and is hottest at the cathode. The operator must be guided by the appearance of the electrolyte at the cathode. There should be a rosette-like spot with radial markings here; if the stick of metal is pulled out too fast, this spot becomes almost white hot, and if the metal is not at once lowered, an arc forms, and part of the metal is melted off and lost. If the stick is not raised fast enough, the spot becomes less noticeable, and spongy metal deposits below the surface, causing losses. When the electrolysis was well under way, new electrolyte was added in small portions, taking care to make these additions as continuous as possible, and in such a spot that the convection currents carried the cold chloride away from the metal. Table I. shows the efficiency obtained.

TABLE I.

Run No.	Time Mins.	Amperes.	Volts.	Weight Grms.	Efficiency. Per cent.
1.	60	74·45	18·3	30·8	55·3
2.	60	73·9	21·4	25	45·2
3.	60	74·2	21	43·5	78·4
4.	38	73·2	26	27	77·8
5.	32	73·1	24·4	26·5	90·7
6.	30	71·5	25·5	24	89·8
7.	27	70·4	33	21·5	90·5
8.	30	69·66	28	26	100
9.	34	52·54	34	21·6	97
10.	36	68·75	31	31	100·5

The sticks of metal were cleaned by hammering off the crust on the outside, and then placing them in absolute alcohol for twenty-four hours to remove the rest of the chloride. When taken out of the alcohol, the sticks were always clean, though covered by a thin coat of oxide. They were dried by burning off the alcohol, and weighed. The current was, of course, not absolutely constant, so there is a possible error of 1 or 2 per cent in the efficiency as calculated, but the results are sufficiently accurate for practical purposes.

Since Ruff and Plato (*Ber.*, 1902, xxxv., 3612; 1903, xxxvi., 491; D.R.P., 153,171; *Chem. Centr.*, 1904, ii., 802), Muthmann (*Zeit. Elektrochem.*, 1904, x., 508), and Woehler (*Zeit. Elektrochem.*, 1905, xi., 612) have recommended the use of a mixture of the chloride and fluoride as the electrolyte, we decided to try it and see if it offered any advantages. The fluorspar was first partially purified by treatment with concentrated hydrochloric acid to remove iron. It was mixed with the chloride in the proportion of 16·5 parts to 100, as recommended by Ruff and Plato. A new crucible was made for use with this electrolyte, having the same size as the other, but a different arrangement of the water-cooling. The bottom of the crucible was turned out on the lathe so as to fit loosely over the hollow brass cooling cylinder of the Borchers furnace for the electrolysis of fused salts ("Die Elektrische Oefen," 1907 ed., p. 35). The crucible was then turned upside down, this space filled with a strong copper sulphate solution, and copper deposited until the cylinder would not enter the space. The copper was now turned out on the lathe to fit the cylinder, and the whole of the outside of the crucible and cylinder protected from the air by a coat of Portland cement and carborundum fire-sand, held in place, as before, by a tin form. The contact being made through the water-cooling cylinder, was kept cool and did not burn away, as the other crucible did in the course of time. A more complete protection of the outside of the crucible was also possible.

With this crucible and the above-mentioned electrolyte a new series of runs was made. Considerable trouble was found in making smooth solid sticks of metal with this electrolyte. The particular advantage of this mixture is supposed to be its low melting-point (660°). This appears to us to be a disadvantage, as the bath must be worked at a temperature of nearly 750° in order to get a solid stick of metal, and the bath is so fluid at the working temperature that convection currents are more violent and more likely to sweep away the metal from the end of the stick, forming an arc. We had a great deal of trouble from this cause. Reduction of the current did not bring the desired result, as the efficiency decreased markedly (Run No. 6, Table II.). The results obtained are shown in Table II.

TABLE II.

Run. No.	Time. Mins.	Ampères.	Volts.	Weight. Grms.	Efficiency. Per cent.
1.	30	42	—	15	95·5
2.	32·5	41·5	31	15	89·2
2.	42	53·9	37	27	95·7
4.	35	45·6	31·3	12·8	64·4
5.	9	54·9	26	5	81·2
6.	41	31·9	30	5	30·6
7.	45	52·1	29·5	18	61·6
8.	45	53·5	30·7	26	86·6
9.	46	69·3	31·4	29·4	74
10.	40	52·7	34	22·6	86
11.	35	53·5	30·8	20	85·5

During the runs with this electrolyte only the chloride was added, it being assumed that the fluoride would not be decomposed. However, at the close of these experiments a sample from the top of the melt showed only 2·21 per cent of insoluble matter, so, evidently, much of the fluoride had been lost. This loss was probably largely mechanical and due to the violent spattering of the electrolyte; it was noticed that a great deal more of the fine dust from the electrolyte collected on the crucible and its surroundings with this than with the simple chloride electrolyte.

We also took samples from the electrolyte in the lower part of the crucible, which had been kept frozen during the electrolysis by the cooling coil, and so, presumably, retained its original composition, and attempted to isolate the fluochloride of calcium described by Poulenc (*Ann. Chim. Phys.*, 1894, [7], ii., 5) and Defacqs (*Ann. Chim. Phys.*, 1904, [8], i., 337; *Comptes Rendus*, 1903, cxxxvii., 1251; *Journ. Chem. Soc.*, 1904, lxxxvi., [2], 123), but found none of it.

From our experience with both electrolytes we believe that the plain chloride is a little more satisfactory than the mixture of the chloride and fluoride in point of efficiency, and decidedly easier to manipulate. We have shown that satisfactorily high efficiencies can be obtained with it, and that efficiency is more largely a matter of careful regulation of conditions than anything else.—*Chemical Engineer*, xii., No. 5.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

December 20th, 1910.

Sixth Annual Exhibition of Electrical, Optical, and other Physical Apparatus.

The sixth Annual Exhibition was held at the Imperial College of Science at South Kensington. These Exhibitions have been growing in magnitude and value since their commencement six years ago, and this last effort has certainly established a record for importance. Some thirty-six firms were represented, and no pains were spared to make the exhibits interesting and instructive. In addition to this demonstrations were given both in the afternoon and evening by Professors J. A. Fleming, Silvanus P. Thompson, and R. W. Wood. The attendance was very good, and was maintained up to a late hour.

The Council of the Physical Society are acting wisely in not allowing these "Exhibition Evenings" to become merely occasions for manufacturers to show their goods, and the demonstration of results and researches by leading physicists of the day, combined with the latest novelties in apparatus by our most active manufacturers, make the occasion of importance, as, in addition to the general interest, they bring manufacturers and workers together to the mutual advantage of both. It is impossible, as well as unnecessary, to enumerate all the exhibits, but we will draw attention to a few of the most novel :—

Among the exhibits of Messrs. R. and J. Beck was the Beck-Gordon Lamp for microscopical illumination. This is a device by which the light from an incandescent mantle or electric filament can be made to give a field of light with a perfectly even area of illumination. A silvered glass cylinder several inches long is mounted in front of the light, which being totally reflected along the sides emerges as a practically homogeneous disc of light. The same firm had also a number of Thorp Diffraction Gratings (celluloid casts from original Rowland rulings). These were of great beauty, and are said to be equal to the originals, and can be produced at moderate cost.

The Cambridge Scientific Instrument Company had a number of novelties, among others Prof. C. T. R. Wilson's Tilted Gold Leaf Electroscope. During the evening a demonstration of the sensitiveness of this beautiful little instrument was given by Dr. G. W. C. Kaye, of the National Physical Laboratory, who showed the electrification due to the splashing of mercury.

Messrs. C. F. Casella and Co. showed a novel form of Barometer with a tube of india-rubber, which could be coiled up and packed away in a bag when not in use.

Messrs. Cossor and Co., the well-known tube makers, showed a new form of X-ray Tube, designed to carry heavy currents. The platinum anticathode is mounted on a massive copper rod, which projects outside the tube, ending in a multiple fin radiator to dissipate the heat formed at the target. The device for regulating the vacuum consisted in a side tube containing asbestos cloth, which is said to liberate a copious volume of dry air when in action.

Messrs. Evershed and Vignoles demonstrated the action of the new Dionic Water Tube. It is an original device for quickly and accurately measuring the electrical resistance of a volume of water and is likely to have a wide range of usefulness; it can be used for measuring the hardness of water, the leakage of cooling water into surface condensers, sewage pollution of rivers, and many other purposes. In the demonstration given a beaker of distilled water gave a reading of 20°; the addition of one drop of sea-water sent the reading up to 80°. A great number of tests have been made of various waters; distilled water varied from 0·2° in the case of a specially pure sample prepared by Kohlrausch to 14° in a sample from a London retail chemist. Water from public supply Companies ranged from Loch Katrine water 34° to West Middlesex London supply 390°, while sea-water taken off Harwich and the Isle of Wight gave 50,000. Of course the instrument will not indicate the nature of the impurity, but one obvious application is to obtain a continuous record of the condition of a water supply. Any abnormal contamination would be at once recorded and could be investigated.

Messrs. Griffin and Sons, amongst other novelties, showed a new mechanically worked Mercurial Pump of very simple construction. A vacuum tube about 14 inches long and 1½ ins. in diameter was exhausted so as to give full green phosphorescence in a few minutes. The pump was fitted with a novel form of McLeod gauge, in which the capacity chamber was replaced by a coiled glass tube of several convolutions about 6 inches in diameter fitted to the pump by a ground joint. The observation was made by trapping a plug of mercury in this tube and rotating it so as to cause the mercury to compress the gas into the measuring tube at the end.

Messrs. Adam Hilger and Co. gave a demonstration of Prof. Wood's method of showing the anomalous dispersion of sodium vapour with great success.

Messrs. Newton and Co. had a new form of Mercury Interrupter for Induction Coils known as the "Dessauer" Break. This is said to be an improvement upon the various gas mercury interrupters now in general use; it gives a very rapid and clean break, and will pass a heavy current, while the construction is simple and unlikely to get out of order. The effect upon one of their "Instanta" coils was to produce a very thick flame-like discharge under perfect control.

One of the newest things in the Exhibition was a small continuous Current Transformer invented by Mr. Leslie Miller of Hatton Garden. At present this little apparatus has only been produced in one form, but it bids fair to have a wide application. The present instrument, in the form of a polished teak box about 10 inches square, can be fitted to any continuous current lamp plug, and takes about half an ampère, and converts it into a low voltage alternating current of about 10 ampères, useful for medical cautery or lighting small lamps, &c. The current can be regulated at will, and the efficiency is said to be very high, certainly above 80 per cent. This apparatus is capable of great development.

Another novelty, shown by Messrs. Wright and Co., was a new Spark Coil Apparatus by Prof. Wilson. It consists of a special form of spark coil with an inductance and an interrupter driven by a small motor. The current was taken from an ordinary lamp fitting, and although the coil looked almost a toy compared with the gigantic machines now in common use, a 5-inch bulb was fully illuminated and gave a very steady and bright green illumination.

Messrs. Carl Zeiss and Messrs. E. Litz both showed beautifully arranged projection apparatus. The latter firm have introduced a quick change instrument by which the change can be made from high power microscopical projection to lantern slides or opaque objects in a few seconds.

Tea and coffee were served, and the convenience of the rooms and staff of the Imperial College of Science added much to the success of the evening.

ROYAL PHOTOGRAPHIC SOCIETY.

Dr. W. Scheffer, the well-known photo chemist and microscopist of Berlin, gave a demonstration of his microscopic researches upon the gelatin film of dry plates before the Royal Photographic Society on December 20th. His aim had been, he said, to discover microscopically, using a magnification of 2000 times, the first physical traces of photographic development. Premising that his physical explanations did not touch in any way upon the chemical theory of the latent image, he said that after an ordinary exposure such as one would give in taking a photograph, and a very brief development with a diluted developer, some of the silver grains in a plate were observed to be projecting fine tiny filaments. These filaments, which in some cases proceeded from a nebulous halo surrounding the grain, and in others from the grain itself, were in reality the first visible traces of the developing process. On carrying development further the developed grain would be found to increase in size and the filaments to become thicker. Certain of the grains, however, had no filaments, and these grains became increasingly delicate as development proceeded, and finally entirely disappeared. The evident function of these filamentless grains of a plate, said Dr. Scheffer, was to act as a nourishment for the black developed grains. As a matter of fact there were two kinds of grains in the plate; the first, the original grains which went directly to form the photographic image, and the second, the nourishing grains, which fed them.

He then brought out the different effects produced by variations in exposure and development. In a plate which had received the correct or optimum exposure for a given development, practically all the nourishing grains disappeared after the developing process, and the formation of black developed grains was at its maximum. Over-exposure entailed an over-production of the original grains bearing filaments, but these grains did not undergo much change in development, and there was a deficiency of nourishing grains. In a plate developed with diluted developer, as compared with one developed with a concentrated developer, many of the nourishing grains were left quite untouched. In the process of intensification of a plate no new grains were formed, but every black developed grain gained something in mass. In the case of reduction with ammonium persulphate those grains which belonged to a portion of the plate fully developed disappeared almost entirely, while others belonging to a portion which had had a shorter development did not disappear, but something like a wall was formed around them to protect them from the persulphate.

The cutting of square sections through the film led to the unravelling of many obscure photographic processes. The photo micrograph of the section of an under-exposed film showed that only the upper part of the gelatin was filled with black developed grain. With the longer exposure the masses of grain which had been developed were observed to go down through the whole film to the glass. The thickness of the layer of black developed grain was an exponential function of exposure. In the under-developed plate also the upper layers of the film only showed black developed grain, whereas with the same exposure but a longer development the masses, obeying the laws of diffusion and mass action, penetrated down to the deeper layers of the film. The same topographical phenomena were observed in comparative work upon ammonium persulphate and Farmer's reducer. In the latter there was a sharp cut limit of action in the film. Farmer's reducer acted only in the upper part of the film and left the deeper layers untouched. Ammonium persulphate, on the other hand, affected all the grains from the top of the film to the bottom. If the velocity of action was great as compared with the velocity of diffusion, the reducer, as in the case of Farmer's, penetrated slowly and acted quickly. If the conditions were reversed, as in ammonium persulphate, there was quick penetration and comparatively slow action. Consequently, in the latter case, the grains from the top to the bottom were affected, no matter where they lay in the film.

NOTICES OF BOOKS.

The Fats. By J. B. Leathes, M.A., M.B., F.R.C.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1910.

This monograph is intended for the use both of physiologists and chemists who are more particularly interested in biology, and it lays emphasis upon the still unsolved problems which are awaiting the attention of trained chemists who have some knowledge of biology. The chemistry and composition of the fatty acids, their alcohols, and fatty acid esters are first fully treated, and methods of extracting them from the tissues and estimating them are then dealt with, while the processes employed in the study of them in the laboratory are described in detail. The fourth and last section of the book is devoted to the physiology of the fats and the part they play in vital phenomena, and although the book gives an excellent critical survey of the work that has already been done on this subject, it is very apparent that there is need for much further investigation, and the author shows clearly the exact directions in which more work must be performed before definite advances can be made in this branch of animal and vegetable chemistry.

An Introduction to the Study of Metallurgy. By Sir W. C. Roberts-Austen, K.C.B., D.C.L., D.Sc., F.R.S. Sixth Edition, revised and enlarged by F. W. Harbord, A.R.S.M., F.I.C. London: Charles Griffin and Company, Ltd. 1910.

The sixth edition of this valuable treatise on metallurgy, the merits of which have long been known to students, teachers, and practical men, has been thoroughly revised by one of Sir W. Roberts-Austen's former pupils; it has been found desirable to make a considerable number of alterations and additions, of which the most important are as follows:—The preparation of a special chapter upon alloys and the fuller treatment of the thermic properties of alloys other than steel; also the discussion of the recent rapid advance of knowledge of the theory and practice of pyrometry, in which new and accurate methods and instruments have recently been perfected. Metallography is also treated much more fully and completely, and many new types of furnaces are described, the chapters on fuels and furnaces having both undergone considerable alterations. Excellent bibliographies are appended to some of the chapters, and the text-book will clearly long retain its position as one of the foremost on metallurgy in the language.

Fire Tests with Textiles. London: The British Prevention Committee. 1910.

The British Fire Prevention Committee has done a valuable work in investigating the inflammability of flannelettes and other textiles, and the results of their investigations ought to be made as widely known as possible. The object of the experiments was two-fold. Firstly, to obtain reliable data as to the relative inflammability of various materials, and to ascertain the effect of treating flannelette with a view of reducing its tendency to ignite; and, secondly, to work out the details of a trustworthy and simple standard test. For these purposes over 450 experiments were performed, and hence the conditions which should be fulfilled by a sample if it is to regarded as non-inflammable were determined. The full results of all the tests are described, and many of them are illustrated by photographs, which show very strikingly the great difference between flannelette and other textiles as regards inflammability, and also the marked effect of treating flannelette by the "non-flam" process.

The Chemists' Pocket Manual. By Richard K. Meade, M.S. Second Edition. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1910.

This pocket manual is designed more particularly for the use of the engineering and works' chemist, and contains all the tables and data which there is any likelihood of his requiring. Moreover, there are full descriptions of the quickest and most accurate methods of determining physical constants and of the usual analytical processes for the examination of metallurgical and other products.

Bell's Sale of Food and Drugs Act. Fifth Edition. By Charles F. Lloyd. London: Butterworth and Co.: Shaw and Sons. 1910.

The fifth edition of this book contains all the Acts relating to the Sale of Foods and Drugs which have been passed between the years 1875—1907, with copious explanatory notes on them and on all cases bearing upon them. The chemical notes have been thoroughly revised by Mr. R. A. Robinson, and a number of circular letters issued by different government departments on matters of practical importance connected with the sale of foods are reproduced. Some of the commoner methods of adulteration of articles of food are discussed, and the book will be found a concise and useful work of reference by analysts and manufacturers.

Photography in Colours. A Text-book for Amateurs, with a Chapter on Kinematography in the Colours of Nature. By George Lindsay Johnson, M.A., M.D., B.S., F.R.C.S. With eight full page Plates in colour. London: Ward and Co. 1910.

Very great advance has recently been made in the preparation of photographs in natural colours, and the most recent triumph has been the production of kinematographic pictures in which the combination of movement and coloration give an astonishingly life-like effect. These results are of great interest and value from a spectacular point of view, and the highly interesting lecture given by Prof. Stirling during the last meeting of the British Association demonstrated the value of the kinematograph as an aid in the study and teaching of natural history. Since the publication of the author's previous work on colour photography the advance has been so great that it has been found necessary to re-write the subject, and the modest little book before us, although written for the amateur, is in reality a thorough elaboration of practically all that has been done upon the subject to the present time. Commencing with "Historical Notes" the evolution of colour photography is traced through the work of Goethe, Zenker, Lippmann, Young, Helmholtz, and Ives, and a whole chapter, well illustrated, is devoted to the physics of the eye, colour vision, and colour blindness. This chapter is particularly valuable; as coming from the pen of a properly qualified man, it places subsequent exposition of the science upon a thoroughly sound basis, and enables the amateur the more readily to grasp the meaning of the various operations that he will have to carry out in the preparation of colour pictures. Up to Chapter VI. the book is devoted to the enumeration and explanation of the various discoveries that have led up to or are involved in the present day work, and numerous illustrations and diagrams are given to render the explanations as clear as possible. Chapters VII. and VIII. deal with the practical working of the various present day processes, and give elaborate and valuable details that show that the author is himself an enthusiastic worker on the subject. Chapter IX. treats of kinematography in natural colours, and shows the advance that has been made, and indicates the possibilities of developments in the near future. On the whole the book will prove invaluable to all who are working on this fascinating subject, and its perusal is likely to encourage many who have hesitated for want of knowledge to know just where to begin.

The Denver Fire-clay Company's Catalogue of Assayers' and Chemists' Supplies.

This fully illustrated catalogue contains many pieces of apparatus not generally found in the lists of similar manufacturers in this country. The most important part is probably that devoted to chemical balances, and many novelties are shown. Most of the precision balances are of the non-column type, where the pointer is above instead of below the knife-edges; advantage of freedom from the effects of air currents is claimed for this method of construction. As might be expected in a Crucible Company much attention has been given to assaying apparatus, and several novelties are shown in crushing and grinding machines. Some new and convenient forms of gas and petroleum furnaces are listed, and the prices compare favourable with similar apparatus obtainable in this country. The book ends with a list of chemicals and reagents.

Griffin's Scientific Handicraft. Fourteenth Edition. London: Griffin and Sons.

The issue of an illustrated catalogue of 1020 pages is no mean task, and Messrs. Griffin and Sons are to be congratulated on having included the description of all their manufactures in one volume. It has been brought quite up to date; this is particularly noticeable in the section devoted to furnaces, radiation pyrometers, &c., where the latest electrical devices for obtaining and measuring high temperatures are shown. We may safely say that all that is needed in the way of apparatus for scientific research or teaching can be found in the book.

The activity of late years in the elaboration and manufacture of science apparatus has made the issue of catalogues of this kind by dealers an absolute necessity, and it has to be done with the consciousness that in a very few years many of the devices shown will be both obselete and unneeded. This unfortunately cannot be helped, and we are quite sure that the fourteenth edition of "Scientific Handicraft" will be fully appreciated by all interested in the advance of science.

The Scientist's Reference Book and Diary. Manchester: Messrs. Woolley, Sons, and Co.

The above diary is in narrow pocket-book form, and is Z shape to open on two sides, practically forming two separate books; one side is the usual calendar, each day of the year marked in good bold type, with Letts and Co.'s Self-opening Memo Tablet; the other side contains a plain ruled memorandum book and a very complete Reference Book of some 96 pages. It appears to be a collection of practically all that can be put into a book of this description; in fact, a miniature encyclopædia. Fortunately there is a good index, so that it is quite easy to turn up any reference in a moment, from a dissertation upon the Abdominal Cavity to the Signs of the Zodiac.

It is an exceedingly handy pocket-book, and the price in red leather is 1s. 6d., and in morocco 2s. 6d.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 19, November 7, 1910.

Progressive Phosphorescence at a Low Temperature.—J. de Kowalski.—At the ordinary temperature benzene and its derivatives exhibit an ultra-violet fluorescence. When the temperature is lowered to $-135°$ the solutions remain liquid but become more viscous, and the fluorescence extends towards the red, so that it becomes visible, although at the ordinary temperature it is invisible. At about $-135°$ the viscous sclutions become solid, and

below the temperature of solidification phosphorescence appears. If the substance is exposed for a very short time to the action of light a bright phosphorescence of short duration appears, and its spectrum is almost identical with the fluorescence spectrum. If the exposure to the source of light is continued it will be seen that fine bands are superposed on the broad fluorescence bands, and their intensity increases with the duration of the exposure up to a limiting value. The emission spectrum of this progressive phosphorescence of an alcoholic solution is a function of the dissolved substance and varies slightly with the concentration of the solution. The bands of its spectrum differ from those of the instantaneous phosphorescence, and the relative intensity of different bands depends upon the temperature and the source of light employed. For every substance there is a temperature above which progressive phosphorescence does not appear.

Preparation of Crystallised Strontium.—A. Guntz and M. Galliot. — Finely powdered strontia is mixed with aluminium in the proportion given by the equation $3SrO + Al_2 = 3Sr + Al_2O_3$. It is then heated in a steel tube to 1000°, and a vacuum is made in the porcelain tube in which it is placed, and thus about 75 per cent of the strontium used is obtained in the crystalline form.

Tetranitromethane.—E. Berger.—Tetranitromethane can be obtained by the nitration of acetic anhydride if the reaction is not allowed to proceed too quickly, the temperature does not exceed 70°, and the reagents are used in the proportion of 160 grms. of pure nitric acid, 100 grms. of crystallised acetic acid, and 290 grms. of acetic anhydride. The density of tetranitromethane is 1·620 at 22°. It distils at 124—125° under 750 mm. pressure, decomposing very slightly with production of nitrous vapours, and at 21—23° under 22 mm. pressure without decomposition. Its boiling-point under 22 mm. pressure is 45—47°. When reduced by aluminium amalgam in a neutral medium it yields the same products as in an acid medium – nitrogen, ammonia, and methylamine, but no polyamines. Its heat of formation from its elements is +7 cals.

Influence of Nitrates on Alcoholic Ferments.—E. Kayser. – Fermentation is more complete in presence of manganous nitrate, and there seems to be a maximum amount of salt which induces the maximum amount of diastatic activity for each kind of yeast. Too great a quantity of nitrate hinders fermentation. Manganese nitrate acts more energetically than an equal amount of potassium nitrate.

Purification of Starch.—G. Malfitano and A. N. Moschkoff.—Starch may be freed from its mineral impurities by heating with pure water, decanting off the liquid, and allowing it to congeal in a nickel vessel and then letting it melt; a liquid is thus obtained which contains the greater part of the salts and very little starch, the latter remaining in the form of flakes, which may be separated by centrifugation. The repetition of this process removes practically all the mineral matter from the starch.

MISCELLANEOUS.

Society of Public Analysts, &c.—The Anniversary Dinner of the Society will be held on Tuesday, January 31st, at the Trocadero Restaurant, Piccadilly, W.

Chemical Engineering and Industries Exhibition. —Formation of Committees in Glasgow and Manchester.—Considerable progress is being made with the arrangements for the forthcoming Chemical Engineering and Industries Exhibition to be held at the Agricultural Hall next May. The Hon. Advisory Council (of which the Chairman is Mr. Walter F. Reid, President of the Society of Chemical Industry) have decided to arrange Local Committees in the chief centres, and during the past week Committees have been formed in Glasgow and Manchester.

The first meeting of the Glasgow Committee was held recently at St. Enoch's Hotel, the following gentlemen being present: Prof. A. Campion, Prof. Thos. Gray, and Prof. G. G. Henderson, Technical College; F. W. Harris, Corporation Chemical Department; D. Perry (Perry and Hope, Ltd.); Andrew Macdonald; Prof. John Ferguson and Prof. Cecil H. Desch, the University; John Traquair (W. Wotherspoon, Ltd.); John Shanks (Shanks and Co., Ltd.); W. D. Bost; W. Hatrick (W. and R. Hatrick and Co.); F. W. Bridges. Mr. F. W. Bridges, the Organising Secretary and Manager of the Exhibition, explained at some length the object and scope of the Exhibition, and the steps which had been taken up to the present by the Hon. Advisory Council to ensure the success of the Exhibition—the first of its kind. He also mentioned that a considerable number of applications for space had been received from leading firms connected with various branches of chemical industry, and the Council were desirous that Scottish firms would be well represented at the Exhibition. At the unanimous wish of those present Prof. G. G. Henderson accepted the position of Chairman of the Committee, and it was decided to hold a further meeting at the Technical College in January, 1911, and in the meantime to considerably strengthen the Committee, as it was considered most desirable that this Exhibition, which is calculated to benefit considerably the chemical industries, should be well supported by engineers and others connected with the chemical industry. A similar meeting was also held at the Midland Hotel, Manchester, those present including:—Dr. Hans Benfey; W. H. Coleman; Jul. Hubner, Secretary Manchester Section, Society of Chemical Industry; W. Beaumont Hart, Manchester Laboratory; J. H. Hoseason (Hough, Hoseason, and Co.); R. H. Clayton, Chairman Manchester Section, Society of Chemical Industry; Chas. Dreyfus (Clayton Aniline Co., Ltd.); S. W. Royse (S. W. Royse and Co.); F. W. Bridges; Mr. Bridges, Organising Secretary and Manager. On the proposition of Prof. Dreyfus, Mr. S. W. Royse was unanimously elected Chairman of the Manchester Committee. The project commended itself favourably to all present, the opinion being freely expressed that such an Exhibition as this was wanted and would do much good to the whole industry. A large number of names were suggested of gentlemen to be invited to join the Committee, and it was agreed to hold a further meeting at the Chamber of Commerce on January 11th, 1911, when various other plans would be discussed with the view to the chemical industries of Manchester and district being well to the front at such an important Exhibition.

NOTES AND QUERIES.

Celluloid in a Dangerous Form.—The presence of celluloid-faced paper goods in an almost indiscernible condition calls for notice. A white papier maché celluloid can be used to face these goods, and in large quantities, or where placed in the immediate neighbourhood of inflammable goods, are a source of danger, unless such celluloid-prepared goods are rendered non-inflammable.—J. C. THOMLINSON.

MEETINGS FOR THE WEEK.

TUESDAY, 10th.—Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Sound, Musical and Non-musical" (a Course of Experimental Acoustics), by Prof. Silvanus P. Thompson, F.R.S., &c.

WEDNESDAY, 11th.—Royal Society of Arts, 5. (Juvenile Lectures). "A Study of Splashes, conducted by the Aid of Instantaneous Photography," by Prof. A. M. Worthington, C.B., F.R.S.

THURSDAY, 12th.—Royal Society. "The Absolute Expansion of Mercury," by Prof. H. L. Callendar and H. Moss. "The Density of Nitron (Radiation Emanations) and the Disintegration Theory," by Dr. R. W. Gray and Sir W. Ramsay. "The Charges on Ions in Gases, and some Effects that Influence the Motion of Negative Ions," by J. S. Townsend. "Distribution of Electric Force in the Crookes Dark Space," by F. W. Aston. "The Measurement of End Standards of Length," by Dr. P. E. Shaw.

THE CHEMICAL NEWS.

Vol. CIII., No. 2668.

MESOTHORIUM.

By W. MARCKWALD.

In 1907 O. Hahn (*Berichte*, xl., 1907, 1462, 3304) indirectly proved that thorium, on undergoing radio-active atomic disintegration, was converted into a metabolon, of which the half-constant was about five and a-half years, and which was separated from thorium during the working-up process of the preparation of the element from its ores. He called it *Mesothorium*. Subsequently Hahn detected this substance in the residues. He showed (*Zeit. Phys. Chem.*, ix., 1908, 246) that mesothorium is not directly converted into radio-thorium, but that a short-lived intermediate product, mesothorium II., results (half duration of life = 6·2 hours). Recently Hahn (Lecture at the Meeting of the German Chemical Society, July 11, 1910) succeeded in concentrating the substance to such an extent that its action considerably exceeded that of an equal weight of pure radium salt. The author has not published any details of the chemical properties of mesothorium I., and the method of discovering and preparing it.

A short time ago I received from a chemical works a "radium preparation" which I was to investigate, determining its percentage of radium. It consisted essentially of barium chloride. Judging from its γ-radiation it must have contained more than 1 per cent of radium chloride. But when its power of emanation was investigated it was found that the radium emanation evolved corresponded to only about 0·2 per cent of radium. Further investigation showed that the greater part of the γ-radiation (about 80 per cent) was due to mesothorium II. For if a trace of iron chloride was added to the aqueous solution of the salt and it was then made ammoniacal, the mesothorium II. was precipitated with the iron hydroxide. A strong γ-radiation was emitted by the precipitate, while the barium chloride obtained by evaporating the solution had lost almost the whole of its power of emitting γ-rays. But while the precipitate lost almost all its power of radiation with a half-constant of about six hours, the salt regained the greater part of its power of radiation in a day. The ammoniacal precipitate must thus contain the radio-thorium formed from the mesothorium. As a matter of fact, after the decay of the mesothorium II. there remained a residue which emitted α-rays, and which gave thorium emanation.

In reply to my enquiries the factory informed me that their "radium preparation" had been obtained by working up residues from ores containing uranium and thorium.

Evidently mesothorium is completely analogous to radium from a chemical point of view. I have not yet succeeded in finding a reaction by which it can be separated from barium and radium. On re-crystallisation of the chloride it accumulates with the radium in the difficultly soluble crystallisations.

This complete similarity of the two radio-active elements is very interesting. For up to the present no method has been found of separating by chemical reactions the four elements—thorium, radiothorium, ionium, and uranium X. Now it seems as if another group of radio-active elements of similar properties exists; to this group belong radium and mesothorium, and possibly other metabolons.

The study of the chemical properties of mesothorium reveals a method of preparing it from the residues of the manufacture of thorium. It is an exact reproduction of that by which radium is obtained from uranium ore residues. Of course the mesothorium preparations obtained from monazite must contain radium, owing to the presence of uranium in them, since no method of separating these two substances is known. Moreover, the radium obtained from thorium ores rich in uranium, as, for example, thorianite always contains mesothorium.

As the duration of life of radium is about 300 times that of mesothorium it is very important when studying a "radium preparation" to take into account the possibility of its containing mesothorium. As in the case I have mentioned a useless preparation was sold with the best intentions, there is also the danger of deliberate adulteration. The simplest way to test a radium preparation for mesothorium is to heat it for a short time to drive off the emanation. The preparation must then lose its γ-radiating power after a few hours, completely regaining it only after the lapse of many weeks. Instead of heating it, it can of course be dissolved in water and the solution evaporated. If after the radium emanation has been driven off, and the radium C has been destroyed (which takes a few hours) there is still some γ-radiation, this is due to mesothorium. The ratio of the γ-radiation before and after the treatment is a measure of the proportion of radium and mesothorium in the mixture.—*Berichte*, xliii., 3420.

THE ESTIMATION OF FREE AMMONIA AND AMMONIUM CARBONATE BY TITRATION.

By J. C. THOMLINSON, B.Sc.

In estimating free ammonia and ammonium carbonate in solutions containing an excess of the former a quick volumetric method may be used.

Free ammonia cannot be titrated using phenolphthalein as an indicator, methyl-orange being usually used; however, when it exists in the free state, and as carbonate, by using phenolphthalein first, and titrating until the liquid assumes a transient pink coloration throughout its entire bulk, we can obtain a close approximation as to the amount of ammonium carbonate present, and by then adding methyl-orange and completing the titration estimate the total ammonia.

To prove this a solution was made containing 0·78 grm. free ammonia, NH_3, per 100 cc., and 3·69 grms. ammonium carbonate, $(NH_4)_2CO_3$, per 100 cc.

To 10 cc. of this solution phenolphthalein was added, and when titrated with normal sulphuric acid as the mean of two experiments, 8·1 cc. N. H_2SO_4 were required.

Calculated as ammonium carbonate, $(NH_4)_2CO_3$, this represents 3·42 grms. $(NH_4)_2CO_3$ per 100 cc.

The total ammonia free and existing as carbonate in the test solution made above would be, by calculation, 2·16 grms. per 100 cc.

A further titration after adding methyl-orange to 10 cc. of the liquid already titrated for carbonate gave the total amount of normal sulphuric acid solution required as 12·5 cc., representing 2·1 grms. total ammonia, NH_3, per 100 cc.

Methyl-orange commonly used as an indicator for the titration of free ammonia, although not feasible as an indicator in the presence of free carbon dioxide, can hence be used when there is an excess of ammonia in ammonium carbon solutions, and the reliability of the titration for carbonate for quick and approximate analysis may be judged from the figures given above.

Royal Institution. On Tuesday next, January 17, at 3 o'clock, Prof. F. W. Mott begins a course of six lectures at the Royal Institution on "Heredity." On Thursday, January 19, at the same hour, the Astronomer Royal, Mr. F. W. Dyson, delivers the first of three lectures on "Recent Progress in Astronomy"; and on Saturday, January 21, also at 3 o'clock, Mr. Arthur Hassall commences a course of three lectures on "Problems in the Career of the Great Napoleon." The Friday Evening Discourse on January 20 will be delivered by Prof. Sir James Dewar on "Chemical and Physical Change at Low Temperatures"; on January 27, by Prof. William H. Bragg, on "Radio-activity as a Kinetic Theory of a Fourth State of Matter"; and on February 3, by Arthur E. Shipley, on "Grouse Disease."

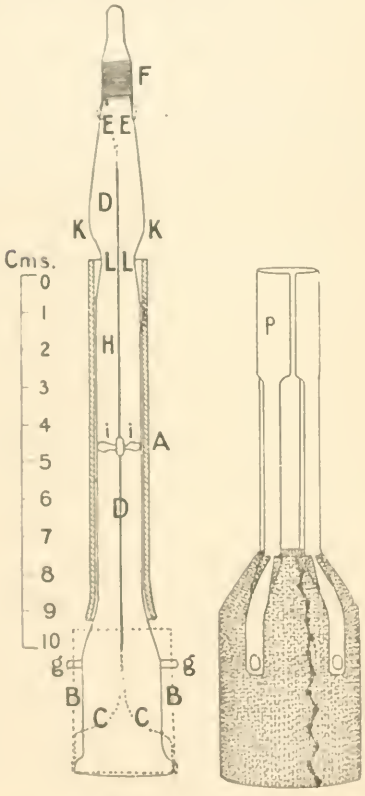
NEW APPARATUS FOR THE RAPID ELECTRO-ANALYTICAL DETERMINATION OF METALS.

A GLASS FRAME ANODE FOR USE WITH SILVER AND NICKEL CATHODES.*

By HENRY J. S. SAND, Ph.D., D.Sc.,
and
WILLIAM M. SMALLEY.

1. *The Apparatus.* By H. J. S. SAND.

In previous publications apparatus for the rapid electro-analytical determination and separation of metals has been described, the principal advantages of which have been set forth in detail (*a*, *Trans. Chem. Soc.*, 1907, xci., 373; *b*, *Trans. Chem. Soc.*, 1908, xciii., 1572; *c*, *Trans. Faraday Soc.*, 1909, v., 159). Attention is here only drawn to the ready adaptability of the apparatus to varying quantities of electrolyte, and to the fact that the efficiency of stirring is independent of the strength of



FIGS. 1*a* AND 1*b*.

current employed. These advantages are absent from all those methods of working in which the current itself is utilised to stir the liquid, and which might otherwise appear attractive from the circumstance that they do away with the expense of a motor.

It was felt, however, that the amount of platinum employed essentially made the apparatus somewhat expensive, and the present communication contains a description of electrodes which may be used in a very considerable number of cases, and which, while retaining as much as possible the features of the former apparatus, only require a minimum amount of platinum. This has been achieved by making the anode wherever possible of glass, and the cathode of metals, such as silver or nickel. An anode made largely of glass has already been described on a former occasion (*loc. cit. a*), but the use of this has been discarded owing to the fact that it was too fragile.

Figs. 1*a* and 1*b* show the apparatus as now employed. The inner electrode *a** is designed to be gripped at the top by the clutch described (*loc. cit. b*), its wide glass stem rotates inside the glass tube A, which latter is gripped by the collar P of the outer electrode, and held by the clamp of one of the stands previously described. In this electrode platinum is only employed in the gauze cylinder B, in the strips of gauze C which lead into the interior of the electrode to the copper wire D, and in the strips E leading out at the top, which are wound over by the platinum wire F. This latter forms a ring against which contact is made by the blocks of the clutch previously referred to.

Attention may be drawn to the following points:—All connections through the glass are made in the manner previously repeatedly referred to, by strips of platinum gauze. In the present case these strips are taken in three-fold thickness at the top, and have a width of not less than 1 cm. below, so that it is possible to pass currents up to 10 ampères through the electrode without endangering it.

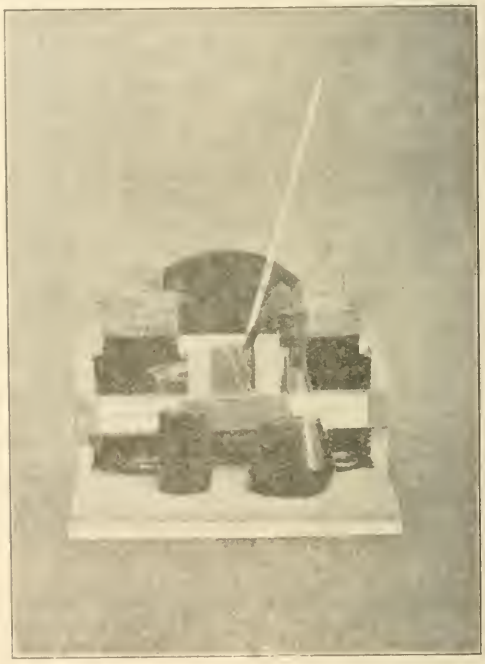


FIG. 2.

The gauze cylinder B is fitted to the bottom of the electrode by blowing the glass against it. At the top, the cylinder stands off from the glass by 2 or 3 mm. in order to allow the gas bubbles which are thrown inwards in consequence of the action of centrifugal force on the liquid, to escape readily. It is held securely by four small protuberances *g* on the glass. The copper wire is held in the interior of the tube H by the enamel support *i*. The platinum wire F is wound in such a manner as to allow its ends to be twisted together at the bottom so that there is no risk of its being pulled off. The stem is widened at K just enough to prevent the tube A from being pulled off, but not enough to hinder the collar P of the outer electrode from being slipped over it. The contraction of the stem at L serves for the purpose of allowing the space between the latter

* A Paper read before the Faraday Society, December 17, 1910.

* The inner electrode was made to my instructions by Universitäts-mechaniker a. D. Fritz Köhler, of Leipzig.

and the guide-tube A to be washed down readily with a few drops of water before disconnecting. The total weight of platinum in this electrode is about 5 grms.

For copper determinations a cathode of silver was used; for zinc determinations one of nickel was employed. In the former case the electrolytic deposit was readily removed at the end of an experiment by means of a hot dilute sulphuric acid solution (1 : 10) to which some hydrogen peroxide (2½ cc. perhydrol per 100 cc.) had been added. The same stripping solution was used a very considerable number of times. The use of a nickel cathode for zinc determinations is not novel, and needs no further comment.

The cathodes do not differ very essentially from those previously described, but great attention has been paid to design them in such a manner that they may be constructed without much trouble with the appliances usually available in a chemical laboratory. The electrode is made only of two principal pieces, viz., (1) the frame, which is cut from a single piece of metal sheet of about half a mm. thickness, and bent into the shape shown, and (2) the gauze. From the latter a cylinder is first constructed, and the final form is obtained by introducing eight small pleats at the top, the size of which can be easily calculated beforehand. These pleats also serve to hold the frame in its place at the top of the gauze, whereas it is fastened below by means of four stout rivets. For the silver cathode fairly coarse gauze (Kahlbaum's coarse gauze) was employed. Owing to the softness and brittleness of the metal it was found desirable to leave no loose ends, but to finish off all the edges in the oxygen blowpipe. It was found easiest to do this by removing a few horizontal threads, and then melting down the projecting ends of the vertical wires. In a similar way the vertical joint in the gauze cylinder was made by removing a few of the vertical wires so that about 5 mm. of the horizontal threads protruded from each end. These latter were then twisted together, and the ends thus obtained were fused down and flattened, thus giving to the joint the appearance shown in the figure. In the case of the nickel cathodes fusing of the loose wires was obviously not feasible, but it was here unnecessary owing to the much stiffer nature of the material. The ends were simply pleated over, and joints made where necessary by fastening with either nickel rivets or wire. The mesh used was 11 per linear cm.

The electrodes may conveniently be formed on suitable glass dummies, which may also be employed to return them to their proper shape if they should accidentally be bent out of form. Copper electrodes may also be made by the identical process employed for those of silver.

With regard to the practical application of these electrodes the following remarks may be made. The numbers given by Mr. Smalley prove that in copper determinations it is possible to obtain as good results with them as with platinum electrodes. There appears, however, to be an appreciable difference in favour of the platinum with regard to the slowness with which the copper goes into solution during the process of disconnecting. Rapid work is therefore desirable during this operation, and, if possible, a large current should be kept passing,

This experience is easy to explain when we remember how very much greater the polarisation capacity of platinum is than that of silver, in consequence of the greater solubility of hydrogen in the former. Harmful couples between the copper and the metal of the cathode will thus arise more quickly in the case of silver than in that of platinum.

A slight blackening at the top of the frame of the silver electrode generally takes place after electrolysis owing to the action of ozone, but apparently does not affect the results appreciably.

The zinc determinations caused no more difficulty with the nickel electrode than with that of platinum. The zinc was removed by warm dilute hydrochloric acid, and the electrode became slightly discoloured after some time without any effect on the results, The glass of the stem of the anode and of the guide-tube is ground down slightly during use, and is found as a turbidity in the exhausted liquids, but no effect of this on the results was noticed.

In conclusion, attention may be drawn to a stand illustrated in Fig. 2, which has been designed to take all the auxiliary apparatus required during analysis. It will be seen that there is a compartment at the back in which the circular block of wood used for raising the tripod is visible. In front of it there is a compartment for the thermometer, and in front of this a compartment for the split cover-glasses. The alcohol and ether jars are held in recesses, by means of a wooden bar, in such a manner that it is impossible to upset them. This bar is held by two round headed screws (not visible), and has two vertical slits which allow it to be slipped into position or removed without undoing the screws. This base of the stand is extended in front to give it more stability, and the wash-bottle and spare beaker required in analysis may conveniently be placed on the extension.

Mention may also be made of the fact that Mr. Smalley has often found it convenient to replace the glass cover-glasses by such cut from pieces of mica.

2. *Results obtained with the foregoing Apparatus in the Analysis of Solutions containing Copper and Zinc. The Determination of Zinc from Citric Acid Solutions.* By W. M. Smalley.

Copper.—A standard solution of copper sulphate was made by dissolving a known weight of purest electrolytic copper (Kahlbaum) in nitric acid, evaporating down to dryness with a small excess of sulphuric acid, and diluting to 1 litre. Twenty-five cc. of the solution thus obtained were calculated to contain 0·3025 grm. of copper, and the electro-analysis with platinum electrodes confirmed 0·3025 grm. Known quantities of this solution were taken for each determination.

To obtain good results warm solutions were always employed. The difficulty of washing the deposit without loss was minimised by having only very small quantities of nitric acid in the electrolyte. At the same time it was found better not to do away with this acid altogether, since, as is well known, it improves the density of the deposit very much. The general mode of working consisted in depositing the bulk of the copper with 10 ampères as long as the solution showed a blue colour, then removing the last traces with 5 ampères until the ferrocyanide or the hydrogen sulphide test showed the liquid to be free from copper, and then increasing the current to 10 ampères during the process of disconnecting. The beaker employed was a narrow form 200 cc. beaker, and the amount of electrolyte used was 110 to 120 cc. (Since these experiments were completed a smaller cathode has been made which may be employed in a 130 cc. beaker with 75 cc. of electrolyte, and which would thus allow the determinations to be completed a little more rapidly than those recorded). Table I. will show that the results obtained under these conditions with varying quantities of copper are practically as good as those usually got by means of platinum electrodes.

Zinc.—For the examination of the deposition of zinc a standard solution was made up by dissolving a known quantity of purest zinc (Kahlbaum) in nitric acid, evaporating off the latter with a small excess of sulphuric acid on the water-bath, and then making up to a known volume. The strength of the solution was checked by electro-analysis according to the acetate method with platinum electrodes, and found correct within the usual limits of error.

Table II. will show that equally accurate results are obtained with the present electrodes by the acetate method as with those of platinum.

The usual procedure was adopted. The solution was generally first made fairly acid with sulphuric acid to cause it to correspond with conditions actually met with in analysis, it was then made alkaline with caustic soda until the precipitate first formed had re-dissolved, and finally acid once more with acetic acid. During analysis a drop

TABLE I.

No	Cu taken. Grm.	Cu found Grm.	Ampères.	Volts.	Temp. °C.	Time. Minutes.	Conc. HNO_3. Cc.	Conc. H_2SO_4. Cc.
1.	0·3025	0·3021	10—5—10	2·9—3·5	55—64	7	0·1	0·7
2.	0·3025	0·3023	10—5—10	2·7—4·0	58—61	6	0·1	0·7
3.	0·3025	0·3023	10—5—8	2·6—4·1	55—58	6	0·1	0·7
4.	0·3025	0·3022	10 5 10	2·8 4·0	50—55	6	0·1	0·7
5.	0·6050	0·6046	10—5—10	2·6—3·7	60—64	9	0·1	0·7
6.	0·9075	0·9075	10—5 10	2·5—3·8	62—65	10	0·1	0·7
7.	0·0605	0·0600	10—5—10	2·8—3·9	50	5	—	0·5
8.	0·0605	0·0603	10—5—10	2·9—4·6	50—70	8	0·1	0·7
9	0·0605	0·0599	10—5—10	2·6 3·8	50—57	7	0·5	0·7
10.	0·0302	0·0300	12—5—10	2·9—4·0	55—61	3	0·1	0·7
11.	0·0302	0·0299	10—5—10	2·7—4·0	50—65	4	0·5	0·5
12.	0·0300	0·0298	10—5—10	3·0—4·2	58—62	4	0·5	0·5

TABLE II.

No.	Zinc Taken. Grm.	Zinc Found. Grm.	Amperes.	Volts.	Temp. °C.	Total amount of— Conc. H_2SO_4. Cc.	NaOH. Grms.	Glacial acetic. Cc.	Time. Mins.
1.	0·3067	0·3050	3	4·6	16	0·75	2	4	20
2.	0·3067	0·3054	3	4·7—5·4	15—18	0·75	2	4	20
3.	0·3067	0·3082	3	4·6	15	0·75	2	4	30
4.	0·3067	0·3065	3	4·7—5·3	17—20	0·75	2	4	30
5.	0·3067	0·3066	3	4·6	18	0·75	2	4	30
6.	0·3067	0·3065	3	4·3	20	0·75	2	4	25
7.	0·3067	0·3064	3	4·8	19	0·75	2	4	25
8.	0·3067	0·3069	3	4·9	15	0·75	2	4	25
9.	0·3067	0·3070	3	4·4	18	0·75	2	4	25

TABLE III.

No	Zinc taken. Grm.	Zinc found Grm.	Ampères.	Volts.	Temp. °C.	Conc. H_2SO_4. Cc.	NaOH. Grms.	Citric acid Grms.	Time. Minutes.	
1.	0·7284	0·7264	5—3	5·6—5·1	21—23	0·75	3·2	5	60	(a)
2.	0·0182	0·0182	5—3	5·9—5·1	20—27	0·75	2	3	50	(a)
3.	0·3642	0·3634	5—3	5·8—5·1	17—22	0·75	2·4	3·6	60	(b)
4.	0·3642	0·3638	5—3	5·6—4·8	20—24	0·75	2·4	3·6	60	(b)
5.	0·7284	0·7314	5—3	5·8—5·2	20—22	0·75	2·4	3·2	65	(b)
6.	0·0182	0·0180	5	5·5	20	0·75	2	3·5	30	(b)
7.	0·0273	0·0279	5	5·8—5·2	20—31	0·75	2	3·5	35	(b)
8.	0·0091	0·0094	5	5·7—5·1	22—29	0·75	2	3·5	25	(b)

(*a*) Platinum copper-coated cathode. (*b*) Nickel cathode.

TABLE IV.

No	Copper taken. Grm.	Copper found. Grm.	Zinc taken. Grms.	Zinc found. Grms.	Ampères.	Volts.	Temp. °C.	Time. Minutes.
1.	0·3025	0·3024			10—5—10	2·9—3·8	55—62	6
			0·36	—	—	—	—	—
2.	0·6050	0·6048			10—5—10	3·0—3·8	50—62	7
			0·7284	0·7262	3	4·1—4·3	28—32	50

was repeatedly tested with litmus-paper, and, if necessary, the solution was maintained acid by the addition of more acetic acid. The temperature was kept low by allowing the beaker to stand in a large crystallising dish containing cold water. The liquid was tested for freedom from zinc after the experiment by means of potassium ferrocyanide. In a few cases it was also electrolysed to constant weight of the deposit.

Citric Acid Solutions.—As there is a distinct tendency with acetate solution for the results to be very slightly high when the liquid is completely exhausted, the following experiments were carried out, in which the acetic acid was replaced by citric (Table III.). The tendency to high results appears to be smaller in this case, but a longer time was usually required to exhaust the electrolyte completely.

Solutions containing both Copper and Zinc.—In Table IV. two experiments solutions were analysed containing both copper and zinc, the identical method being employed which was used for these metals singly.

The amount of acid present in the copper determination of No. 1 was 0·1 cc. nitric and 0·7 cc. sulphuric, in No. 2 it was 0·1 cc. nitric and 0·5 cc. sulphuric. In No. 2 the liquid exhausted of copper was prepared for the determination of zinc by evaporating down on a water-bath with excess of sulphuric acid to expel the nitric; the residue was dissolved in water made strongly alkaline with caustic soda solution until the precipitate first formed had re-dissolved (8 grms. NaOH), and then acid again with citric acid (15 grms.).

The following additional remarks may be made regarding the use of the electrodes. When it was necessary to clean them thoroughly before a first determination, this was done by boiling first with caustic soda solution, and afterwards by treatment with nascent hydrogen, obtained by electrolysing dilute sulphuric acid with a high current density. In the case of the silver electrode an appreciable amount of blackening of the upper part of the frame took place during this process, owing to the production of ozone at the anode. It was found best only to remove as much of this as could be rubbed off with a silk handkerchief, but it was not desirable to remove the black deposit completely by ignition, since this leaves the surface of the silver in a somewhat porous state, in which it is specially liable to further attack by ozone in future determinations.

The method of washing, disconnecting, and drying is practically identical with that used for platinum electrodes

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 15th, 1910.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society in the death of Prof. Dr. Rudolph Fittig on November 19th, and stated that the following telegram of condolence had been forwarded to Herr Fittig :—

"The President, Officers, and Council of the Chemical Society deeply mourn the loss of their distinguished Honorary and Foreign Member, Professor Dr. Rudolph Fittig.—Horace T. Brown, Foreign Secretary."

It was announced that the Faraday Lecture would be delivered by Prof. Theodore W. Richards on June 14th, 1911.

Messrs. H. V. A. Briscoe, H. Leslie F. Buswell, Riko Majima, A. D. Mitchell, and Sidney H. Newman were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Allan, M.A., B.Sc., Ravenscourt, Lerwick, Shetland Isles ; Joseph Bate, 59, Southwood Lane, Highgate, N. ; Joseph Mayson Blackburn, 346, Deane Church Lane, Bolton ; Michael Angelo Fielding, 8, St. Joseph's Place, Cork ; Evan Dalton Griffiths, B.Sc., 9, Wanstead Park Avenue, Manor Park, E. ; Arthur Bennett Hall, 31, Dyer Street, Kirkham ; Charles Herbert Hampshire, B.Sc., 19, Brook Street, Ilkley ; Bernard Grindrod Hough, The Chesnuts, Wardle Road, Sale ; Ernyst Graham Laws, B.A., Alverna, Edith Road Ramsgate ; Ian Gordon Sellar Wink, 27, Panmuir Road, Cottenham Park, Wimbledon, S.W.

Of the following papers, those marked * were read :—

332. "*Studies on Enzyme Action*, Part XV. *The Comparative Influence of Monohydric, C_nH_{2n+1}, Alcohols and other Non electrolytes on Enzymic Activity.*" By Henry E. Armstrong and Edward Frankland Armstrong.

The influence exercised by a number of non-electrolytes in several cases of enzymic change was considered from the point of view of the influence of molecular weight in modifying activity in the case of related compounds.

*333. "*Studies on Eyzyme Action.* Part XVI. *Prunase and Amygdalase ; their Separate Occurrence in Plants.*" By Henry E. Armstrong, Edward Frankland Armstrong, and Edward Horton.

It has been argued in former communications that the hydrolysis of amygdalin by almond emulsin is effected in several stages by distinct enzymes, the contention being that it is first resolved into a molecule of glucose and Fischer's glucoside by the action of amygdalase, Fischer's glucoside being then resolved into glucose and mandelonitrile by the agency of a second enzyme. Sources of the latter enzyme, in which it is unaccompanied by amygdalase, were indicated.

Evidence was adduced from which it was inferred that amygdalin is usually formed in the fruit, probably from Fischer's glucoside formed in the leaves.

*334. "*Studies on Enzyme Action.* Part XVII. *The Distribution of β-Glucases in Plants.*" By Henry E. Armstrong, Edward Frankland Armstrong, and Edward Horton.

A general method of studying the enzymes in plants was described, and examples were given of its application.

*335. "*Studies on Enzyme Action.* Part XVIII. *Linase.*" By Henry E. Armstrong and John Vargas Eyre.

Further examples were given of the application of the method described in Part XVII. to more than a dozen species of *Linum* ; the experiments have been carried out with the object of studying the enzyme characteristic of this family.

Discussion.

Dr. Russell pointed out that some of the leguminous plants mentioned by Prof. Armstrong as being rich in glucoside-splitting enzymes were also known to undergo very rapid fermentation in the animal stomach, which seemed to indicate high enzymic activity in other directions also. He further asked what was the function of the hydrolytic products of the glucosides, and whether it was possible that some of them might act in the plant in the same way as hormones acted in the animal, by controlling certain of the processes going on. When, for example, the reproductive processes began in the plant there set in an alteration in the type of changes taking place, vegetative growth giving place to seed formation. The mechanism bringing about this alteration in the case of animals could hardly be assumed in the case of plants, but it was conceivable that some of the bodies Prof. Armstrong had described might be effective.

In answer to Mr. Hall, Prof. Armstrong said that the amount of enzyme present in the organs of a plant was undoubtedly different at different seasons, and it would be necessary to study plants over the whole period of growth.

In answer to Dr. Russell he said that they had been led to conclude that glucosides were not so much reserve food materials in the ordinary sense of the term, or protective agents, but that, in many cases, the significant constituent exercised a function in the plant similar to that which it exercised when present in human food—that is to say, they served to stimulate enzymic change. It was an interesting fact that seeds of plants rich in glucoside often germinated with extreme readiness, the plant also growing rapidly, as in the case of mustard, for example. The change involved in the ripening of seeds might well be hastened by the rapid separation of hydrogen cyanide, for example, from a cyanophoric glucoside towards the close of the period of growth. The final disappearance of the cyanide from linseed and from vetch seeds was perhaps to be explained in this way. In the case of the banana, the unripe green pod blackened rapidly under the influence of anæsthetics ; in the national ripening process, this change was determined from within the fruit by the liberation of a fruit ether (ethereal salt), and the outward blackening was thus a signal of the completion of inward change.

*336. "*Investigations on the Dependence of Rotatory Power on Chemical Constitution.* Part I. *The Rotations of the Simplest Secondary Alcohols of the Fatty Series.*" By Robert Howson Pickard and Joseph Kenyon.

The resolution of the inactive forms and determinations of the rotatory powers at different temperatures and other properties of the optically active forms of the following alcohols were described :—Methylethylcarbinol, methyl-*n*-propyl-, methyl-*n*-butyl-, methyl-*n*-amyl-, methyl-*n*-hexyl-, methyl-*n*-heptyl, methyl-*n*-octyl-, methyl-*n*-nonyl-, methyl-*n*-decyl-, methyl-*n*-undecyl-, ethyl-*n*-hexyl-, methyl*iso*-butyl-, phenylmethyl-, and phenylethyl-carbinols.

*337. "*The Chemistry of Mesothorium.*" By Frederick Soddy.

Experiments on the mixture of radium and mesothorium with barium sulphate, obtained by adding a barium salt and sulphuric acid to a solution of thorianite in nitric acid, have shown that the separation of mesothorium is not due, as previously has been supposed, to its adsorption by the barium sulphate, but depends on a true chemical analogy between mesothorium and barium of the same kind as exists between barium and radium. The mesothorium could not be concentrated from the barium by chemical methods. By fractional crystallisation of the chlorides, the mesothorium remains with the radium, and can thus be separated from the barium. The proportion between mesothorium and radium is completely unchanged by fractional crystallisation of the chlorides. In the ordinary method used in the manufacture of thorium compounds for dissolving monazite sand, by heating it with excess of sulphuric acid and agitating the product with water, some of the mesothorium remains in the insoluble residue, but

the greater part passes into solution. If a small quantity of a barium compound is mixed with the monazite sand before treatment, practically the whole of the mesothorium is separated with the insoluble residue, none passing into the solution. The part of the residue containing the mesothorium can readily be separated from the heavy unattacked sand by decantation. From this part the mesothorium can be separated by methods similar to those employed in the working up of pitchblende residues for radium. The cases of complete chemical identity between groups of radioactive elements, differing presumably in atomic weight, which now appear to include all the radio active elements of period of average life longer than a year, are in direct conflict with the principle of the periodic law.

338. "*Traube's Molecular Volume Method Applied to Binary Mixtures of Organic Substances.*" By William Rintoul Gelston Atkins.

The compounds and eutectic mixtures described by Philip (*Trans.*, 1903, lxxxiii., 814) were prepared, and their densities determined at or slightly above their melting- or eutectic points respectively. Chloral hydrate was also studied.

In dealing with a compound, the molecular weight is given, according to Traube, by $M = \rho(\Sigma \text{ atomic volumes} + \text{co volume})$, whereas if the calculation of the sum of the molecular weights of the molecules in the material being studied be made, one obtains $M = \rho(\Sigma \text{ atomic volumes} + n \text{ co volumes})$, where n is the number of molecules going to form the supposed compound. From the measure of agreement between the values thus obtained and the theoretical molecular weight of the assumed compound, it is possible to ascertain whether a compound exists or whether the fused mass is merely a mixture, eutectic or otherwise.

In the accompanying table are given the calculated molecular weights obtained from the relation :—

$$M = \rho t\,[\Sigma \text{ at. vol, } + \text{co.-vol. at } 0^\circ\,(1 + \alpha t)]$$

for a compound, and—

$$M = \rho t\,[\Sigma \text{ at. vol. } + n \text{ co.-vol. at } 0^\circ\,(1 + \alpha t)],$$

using the values for the constants given by Reychler ("Outlines of Physical Chemistry," p. 68), and by Smiles ("Chemical Constitution and Some Physical Properties," p. 143), where α is the coefficient of expansion of a gas (1).

Freezing-point curve shows eutectic-point at 15·6°. Traube's method reveals, at the most, slight association (2).

Both methods point to a considerably dissociated compound, m. p. 28·8° (3).

Both methods show a considerably dissociated compound, m. p. 28·5° or 30·0°, according to which crystalline form was present (4).

Freezing point curve shows eutectic-point at 18·1°. Traube's method points to the opposite conclusion (5).

Both methods point to a considerably dissociated compound, m. p. 61° (6).

Both methods show a greatly dissociated compound (7).

A highly dissociated compound is shown by the freezing-point curve. Traube's method agrees with this, but the results might almost equally well be taken as pointing to slight association among the like molecules (8).

The magnetic rotation and chemical evidence point to a compound, as does the above calculation (9).

Finlay's determinations of the freezing point curves show that this is a mixture. Traube's method indicates a compound.

Thus in seven of the examples the evidence afforded by the various methods is not contradictory, whilst in two cases the results are absolutely at variance. It must, however, be remembered that the values obtained by Traube's method indicate association in the fused mass without distinguishing, for example, whether in No. 2 it is the phenol molecules which are associated with each other and the α-naphthylamine similarly, or whether the phenol and α-naphthylamine molecules combine in a certain percentage of cases. If, however, the latter be the case, it is not easy to see why the association of the phenol should be between one and two when mixed with α-naphthylamine, and between two and three when mixed with carbamide. For the latter conclusion cannot be avoided unless it is supposed that the association of the carbamide in phenol solution is sufficiently high to raise the average of the mixture (phenol, 66 per cent, carbamide 33 per cent, by molecules) to the value found. This is rendered very unlikely, as a determination of the molecular weight of thiocarbamide in phenol (about 1·7 per cent of thiocarbamide by weight) gave a nearly normal value, 87 instead of the theoretical, 76. This result was obtained in an attempt to trace the freezing-point curve of phenol and thiocarbamide to see if a compound similar to the phenol-carbamide compound could be obtained. However, the separation of crystals of what had all the appearance of being thiocarbamide show an eutectic-point at 36·8°, only 3·74° below the melting-point of the pure phenol used. The thiocarbamide present at the eutectic-point amounted to only 4·2 per cent.

Thus it seems fair to conclude that whilst by Traube's method alone it is not possible to decide whether the association is between the like molecules or the unlike, taking other facts into consideration the method may be considered trustworthy for temperatures up to 60° at any rate. Above this the effect of the coefficient α becomes considerable. In view, however, of the very good agreement in the case of chloral hydrate (163·5 calc., and 165·5 theoretical) at 66°, it seems to be quite allowable to use the method at 105° for the thiocarbamide-thiocyanate fused mass. The above evidence for the existence of Philip's compounds in the liquid state receives confirmation from Treitschke's viscosity measurements (*Zeit. Phys. Chem.*, 1907, lviii., 425). These show that the compounds exist as such, but in a largely dissociated condition. Rise of temperature increases the dissociation.

	ρ.	(*a*).	(*b*).	(*c*).
(1) *o*-Nitrophenol and *p*-toluidine	$\rho_{16}/_{15} = 1{\cdot}171$	221	251	246
(2) Phenol and α-naphthylamine	$\rho_{29}/_{15} = 1{\cdot}125$	223	253	237
(3) Phenol and *p*-toluidine	$\rho_{30}/_{15} = 1{\cdot}037$	186	214	201
(4) Phenol and diphenylamine	$\rho_{33}/_{15} = 1{\cdot}075$	266	294	263
(5) Phenol (2 mols.) and carbamide (1 mol.)	$\rho_{61}/_{15} = 1{\cdot}104$	216	264	244
(6) Aniline and *p*-cresol	$\rho_{24}/_{15} = 1{\cdot}032$	185	212	201
(7) *p*-Toluidine and α-naphthol	$\rho_{54}/_{15} = 1{\cdot}075$	229	260	251
(8) Chloral hydrate	$\rho_{66}/_{4} = 1{\cdot}575$	163·5	216·6	165·5
(9) Ammonium thiocyanate (3 mols.) and thiocarbamide (1 mol.)	$\rho_{105}/_{15} = 1{\cdot}231$	298	423	304

(*a*) M as compound. (*b*) M as mixture. (*c*) M theoretical.

339. "*Hydroxycodeine*; *a New Alkaloid from Opium.*" By James Johnston Dobbie and Alexander Lauder.

This alkaloid was discovered by Messrs. T. and H. Smith, Edinburgh, in the mother-liquors obtained in the working up of the opium alkaloids after the ordinary alkaloids have been eliminated. It has the formula $C_{18}H_{21}O_4N$, and is a tertiary base. It is soluble in water and the usual organic solvents. So far it has not been obtained in the crystalline condition. On heating, it softens about 40°, and is completely melted at 51°. It is slightly dextrorotatory, and contains one methoxyl group. The *hydrobromide*, $C_{18}H_{21}O_4N,HBr$, crystallises readily from water in large hard prismatic crystals. The *platinichloride* has the formula $(C_{18}H_{21}O_4N)_2,H_2PtCl_6$.

The alkaloid appears to be a hydroxy-derivative of codeine; its absorption spectra agree very closely with those of codeine, and the colour reactions of the two alkaloids are practically identical.

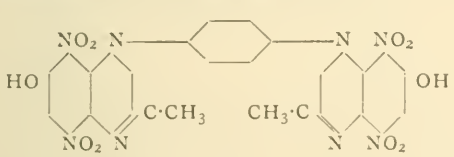
340. "*Studies in the Carbazole Series.*" By Carl Gustav Schwalbe and Salomon Wolff.

The object of this work was to prepare mercaptans of carbazole with the view of converting them into sulphide dyes and sulphonic acids. It was found that in most cases, instead of the required mercaptan being obtained, the derivatives employed were re-converted into carbazole itself. In repeating the preparation of carbazoledisulphonic acid according to Schultz and Hauenstein's method (*Journ. Prakt. Chem.*, 1886, [2], xxxiii., 1907), the authors obtained a disulphonic acid having different properties, giving, for example, a different disulphonyl chloride and disulphonamide. In sulphonating carbazole under various conditions, a monosulphonic acid was never obtained, but disulphonic acids or a mixture of di- and tri-sulphonic acids always resulted. Carbazole is easily sulphonated by 67 per cent sulphuric acid, giving a disulphonic acid, differing from that of Schultz and Hauenstein, and also from the acid mentioned above. On sulphonating 3-nitrocarbazole and subsequent reduction, an amino-disulphonic acid was isolated.

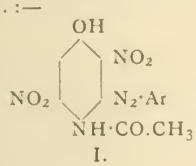
1-*Phenyl*-1 : 2 : 3-*benzotriazole*-5-*sulphonic acid* was prepared by the diazotisation of *o*-aminodiphenylamine-*p*-sulphonic acid. This triazole, on heating, gave carbazole instead of the expected monosulphonic acid.

341. "*Syntheses with Phenol Derivatives containing a Mobile Nitro-group.* Part III. *Complex Iminazoles, Azo-compounds, and Azides.*" By Raphael Meldola and Harold Kuntzen.

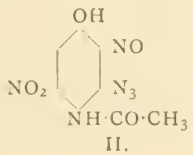
The authors indicated the existence of a new type of bisiminazoles, and described the first member of this series, which is a colloidal substance of the formula—



A further study of the interaction of trinitroacetylaminophenol and aromatic hydrazines has led to the discovery that asymmetric secondary hydrazines are without action, but that primary hydrazines yield azo-compounds of the type I. :—



I.



II.

It was also shown that the trinitro-compound is readily decomposed by sodium azide with the formation of the triazocompound II.

342. "*The Correlation of Viscosity with other Constitutive Properties.*" (Preliminary Note). By Thomas Percy Hilditch and Albert Ernest Dunstan.

The authors have been engaged for some time on an investigation concerning the effects of various constitutive features on the viscosity coefficient in an attempt to bring this property into line with molecular refraction, dispersion, magnetic rotatory power, optical rotatory power, and the like. They have found that, in general, a close parallelism exists between the effects of unsaturation (simple and conjugated) on these diverse properties.

In particular, the result of acetylenic union is invariably to raise the viscosity coefficient, whilst a similar observation was made in general for the ethylenic linking. On the other hand, the saturated compounds in all cases have the lower viscosity, and in most a noticeably greater molecular volume. Various cases of conjugated unsaturation also have been examined, and the authors have found a remarkable exaltation in comparison with the values obtained from unconjugated unsaturated substances.

Symmetrically conjugated compounds have been found to exhibit a still more extraordinary anomaly. As an illustration may be quoted the time of efflux for the following typical cases :—

	Secs.
4-Hydroxy-3-methoxy-1-allylbenzene	2126·0
4-Hydroxy-3 methoxy-1-propenylbenzene ..	8160·0
3 : 4-Methylenedioxy-1-allylbenzene	682·6
3 : 4-Methylenedioxy-1-propenylbenzene ..	1161·8
Ethyl propyl ether	145·2
Ethyl allyl ether..	140·7
Ethyl propargyl ether	206·2

The authors propose to extend this line of work to such cases as ring formation, hydroaromatic and aromatic compounds, spatial propinquity of unsaturated groupings, symmetrical and unsymmetrical substitution in aromatic compounds, and viscosity constants for the various homologous series.

343. "*Physical Properties of Mixtures of Ether and Sulphuric Acid.*" By James Robert Pound.

Mixtures of ether and "100 per cent sulphuric acid" were chiefly used in this investigation; some work was done with ethereal solutions of 95 per cent sulphuric acid. All the experiments were carried out at 30°, and in a few cases also at 20°. In the case of none of the physical properties examined do the solutions obey the "normal mixture" rule. The specific volumes are up to 10 per cent less than the theoretical values. The contraction on mixing is greatest about the equimolecular mixture. The conductivity of the mixtures with "the 100 per cent acid" rises to a maximum for the 89 per cent acid mixture. There is a sharp descent from this maximum to the minimum conductivity, which occurs with the 98 per cent acid mixture. This minimum is similar to that obtained on adding a little water to 100 per cent sulphuric acid. The viscosity curve for the ether-acid mixtures has a maximum at the 67 per cent acid mixture, and closely resembles the corresponding curve for water-sulphuric acid solutions. Over the range from the 59 per cent to the 89 per cent acid mixture, the product of the viscosity and the conductivity varies linearly with the composition. The surface tensions, found by the method of drops, vary linearly with the composition over a large range—from the 20 per cent to the 80 per cent acid mixture. The vapour pressures of the solutions decrease as the percentage of acid increases, the fall of vapour pressure being greatest between the 40 per cent and 50 per cent acid mixture. Here, as in the previous cases mentioned, the curve resembles the corresponding one for water-sulphuric acid mixtures. The actual number or composition of the complexes that are certainly formed in the solutions cannot be given definitely.

344. "*New Syntheses of Thioxanthone and its Derivatives.*" (Preliminary Note). By Samuel Smiles.

In a previous communication (*Trans.*, 1910, xcvii., 1290) it was shown that thioxanthone and its derivatives may be obtained by the condensation of aromatic substances with either *o*-carboxybenzenesulphinic acid or with *o*-thiolbenzoic acid. It has now been found that other four methods are available for the synthesis of these substances :—

1. Condensation of *o*-dithiobenzoic acid with aromatic derivatives in sulphuric acid.

2. Condensation of *m*-hydroxy- or *m*-amino-benzoic acids with (*a*) suitable disulphides, or (*b*) certain sulphinic acids in sulphuric acid.

3. Action of *o*-thiolbenzoic acid on certain quinones, and elimination of water from the product. The three last-named methods yield products the structures of which are known from those of the reagents. These reactions are being studied in detail.

345. "*Cryoscopic, Ebullioscopic, and Association Constants of Trimethylcarbinol.*" By William Ringrose Gelston Atkins.

The cryoscopic constant of trimethylcarbinol was found to have the value E = 128, from which, by van't Hoff's equation, the value for the heat of fusion, $s = 13{\cdot}84$ cal., is obtained. Taking de Forcrand's value, $s = 20{\cdot}98$ cal., E (calc.) = 84·5. The appearance of the solid first in the form of minute needles, which soon change into orthorhombic plates, gives some ground for supposing that the experimental and calculated values of E differ because an unstable crystalline modification is the first to separate out, in which $s = 13{\cdot}84$, whereas $s = 20{\cdot}98$ was determined from the stable form. This unstable form may be the modification which Tammann found to be stable only at high temperatures and pressures.

Boiling-point determinations give E′ = 17·45; calculation from the equations of van't Hoff, Tsakalotos, and Baume gives values ranging from E′ = 18·97 to E′ = 19·78, whilst $dp/d\mathrm{T}$ (calc.) = 28·4.

Calculation from the observed values of γ_t by Ramsay and Shields' equation gives $x = 1{\cdot}388$ from 35° to 47°, and $x = 1{\cdot}304$ from 47° to 80°, whilst Walden's equation gives $x = 1{\cdot}094$ at the boiling-point, 82·5°. Longuinescu's relation gives $x = 1{\cdot}12$ at 30°.

346. "*The Syntheses of* 3-*β-Aminoethylindole and its Formation from Tryptopham.*" (Preliminary Note). By Arthur James Ewins and Patrick Playfair Laidlaw.

Since a number of bases derived from naturally occurring amino-acids have been recently shown to be physiologically active, it was thought desirable to prepare 3-*β*-aminoethylindole, the base corresponding with tryptophan indole-3-α-aminopropionic acid). The base has been obtained in two ways.

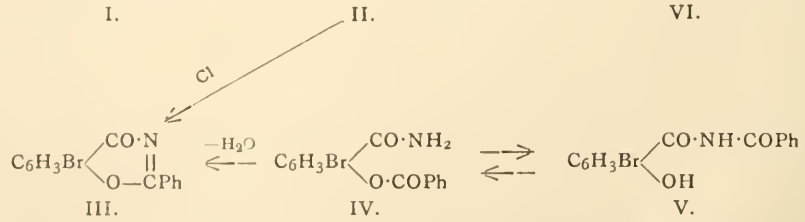
1. By heating together γ-aminobutyrylacetal and phenylhydrazine in presence of zinc chloride. The reaction product, on suitable treatment, gives a good yield of the picrate of the desired base.

2. By submitting tryptophan to the action of putrefactive organisms under conditions similar to those employed by Ackermann (*Zeit. Phys. Chem.*, 1910, lxv., 504) in the preparation of 4-*β*-aminoethylglyoxaline from histidine. A small quantity of a picrate identical in all respects with the synthetic compound was isolated. The base has been found to be physiologically active, producing a rise of blood pressure. The action has, however, yet to be fully worked out.

The details of the synthesis will, it is hoped, shortly be communicated, and experiments are in progress with a view to the production of other indole derivatives by the same process.

347. "6-*Bromo*-2-*Phenyldihydro*-1 : 3-*benzoxazine*-4-*one and Related Derivatives.*" By Ernest Chislett Hughes and Arthur Walsh Titherley.

2-Phenyldihydro-1 : 3-benzoxazine-4-one (I.), on bromination in chloroform solution, yields the 6-*bromo*-derivative (II.) (m. p. 223°), which, with chlorine in benzotrichloride solution at 110°, is dehydrogenated, and gives 6-*bromo*-2-*phenyl*-1 : 3-*benzoxazine*-4-*one* (III.) (m. p. 208°). The latter is also obtained by dehydration of O-*benzoyl*-5-*bromosalicylamide* (IV.) (m. p. 154°) under the catalytic influence of hydrogen chloride, and it suffers ring fission on hydrolysis in presence of alcoholic hydrochloric acid, producing N-*benzoyl*-5-*bromosalicylamide* (V.) (m. p. 249°). O- and N-benzoyl-5-bromosalicylamides show the same reciprocal transformations as the other previously described O- and N-acylsalicylamides, and they have been obtained by similar methods. The dihydro-derivative (II.) has been synthetically obtained from 5-bromosalicylamide and benzaldehyde, into which it decomposes on hydrolysis; whilst on treatment with alkali and pyridin, it re-arranges to a very labile open-chain isomeride, syn-*benzylidene*-5-*bromosalicylamide* (VI.).



348. "*Reactivity of the Halogens in Organic Compounds.* Part V. *Interaction of Esters of the Bromo-substituted Fatty Acids with Silver Nitrate in Alcoholic Solutions.*" By George Senter.

The relative rates with which the bromine is eliminated from the esters of the lower bromo-substituted fatty acids by means of silver nitrate in alcoholic solution have been measured at 49·9°, and in some cases at 26·0°. The results for the higher temperature are summarised in the table, in which k represents the relative velocity-coefficients under comparable conditions :—

Ester.	$k \times 10^4$.
Ethyl bromoacetate	0·208
„ α-bromopropionate	0·085
„ α-bromo*iso*butyrate	0·062
„ α-bromobutyrate	0·038
„ α-bromo*iso*valerate	0·022
Methyl bromopropionate	0·077
Ethyl „ „	0·085
n-Propyl „ „	0·087

Measurements have also been made with methyl alcohol as solvent, and also in mixtures of ethyl alcohol with other solvents. The results were compared with those obtained for the corresponding acids (*Trans.*, 1910, cxvii., 246), and the effect of substitution on the reactivity of the bromine was discussed.

349. "*Attempts to Prepare Glycerides of Amino-acids.*" By Roman Alpern and Charles Weizmann.

The following new compounds were described :—*αα′-Dipropionin*, $C_9H_{16}O_5$, boiling at 170—173°/10 mm. *α-Bromoacetin*, $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_2Br$, a yellow oil boiling at 217–219°/10 mm. *αα′-Diacetoacetin*, $C_{11}H_{16}O_7$, prepared by condensing acetoacetic ester and glycerol in the presence of sulphuric acid, a heavy yellow oil with an odour recalling that of ethyl acetoacetate; it boils at 157—160°/14 mm. *αβ-Dichloroacetoacetin*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2Cl$, a liquid boiling at 103—105°/14 mm. *Ethyl* N-*allylglycine*, $CH_2{:}CH{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, prepared from allylamine and ethyl bromoacetate in ice-cold ethereal solution, a liquid boiling at 74—77°/15 mm.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, January 2nd, 1911.

Mr. E. Grant Hooper in the Chair.

The following papers were read and discussed:—

"*Radiation Errors in Flow Calorimeters.*" By J. H. Coste and B. R. James.

The tacit assumption usually made that losses or gains due to heat exchanges between a gas calorimeter of the flow type and its surroundings are negligible is correct only when the temperature of the water supply approximates closely to that of the surroundings. If this is not the case, it will be found that when water is allowed to circulate through the instrument without lighting the gas the temperature of the outlet water will be different from that of the inlet. If the water supply, as is usual, is of a lower temperature than the surroundings of the calorimeter, heat will be absorbed by the latter and the outlet thermometer will record a higher temperature than the inlet thermometer. Examples showing this are given.

It is shown that the changes were due to radiation rather than to convection.

The error due to absorption or radiation of heat could conceivably be corrected in three ways.

1. By considering the thermometer readings when water is flowing at the desired rate, but no gas burning, as index or zero errors and using the observed increased difference between inlet and outlet.

2. By raising the water to the temperature of the room. This may be done by having a water-tank in the room, or by passing the water through coils of piping heated either by gas or by chemical action.

3. By surrounding the instrument with an annular metal vessel (separated from it by an air space) through which water circulates before reaching the inlet thermometer.

This method has the special advantage that it places the calorimeter in a position where it is not affected by fluctuations of external temperature. This is important when a suitable room of a constant temperature and free from draughts is not available.

The fact that flow calorimeters do not present a homogeneous temperature system renders the computation of errors due to radiation most difficult, so that a reduction of them is the most practical method of minimising their effect.

The results obtained under ordinary winter conditions and by the methods indicated are compared. The uncorrected results are in each case higher than those in which the temperature of the surroundings of the calorimeter and the inlet water have been made to approximate closely. The average difference is about 1 calorie. In summer this would be less.

A Boys calorimeter was used for these experiments. The authors concur with the advice of the American Committee that attention should be paid to the reduction of errors of the kind indicated in all accurate work.

The correction of $\pm\frac{1}{2}$, the difference of temperature of inlet and outlet air used in official testing, appears to correct fairly well errors due to other causes than radiation. The general tendency is for results so corrected to be above the truth. This is not, from a testing point of view, of great importance, since any standards based on such testing would be equally affected by such errors. It is, however, desirable to put on record both the nature and amount of errors due to radiation and the above simple means of reducing them.

"*The Testing of Incandescent Mantles.*" By J. H. Coste and W. E. F. Powney.

The authors describe a system for the comparative examination of incandescent mantles, based on the elimination of those which are of defective strength, by means of the Woodall-Moon machine, which administers a series of equal shocks at equal intervals, causing a vibration in the stem supporting the burner and mantle. After being burnt off and hardened by five minutes burning, upright mantles are expected to stand 1000 shocks and inverted mantles 3000 shocks. Three mantles are tested, and, if any fail to stand 1000 shocks, three more are tested. By testing only up to 1200 and 3600 shocks respectively, one unusually strong mantle is not allowed to compensate for abnormally weak ones, and a failure of one in six is allowed.

Mantles which pass the above test are tested photometrically. Three are burnt for 100 hours on their proper burners, and are then removed to the photometer. The horizontal value is taken for upright mantles, and the average of the values at 0°, 45°, and 90° with the horizon for inverted mantles.

A final selection can be made either by disregarding all with an average illuminating power below a certain amount, and then striking out all with an excessive variation between individuals; or by subtracting from the average illuminating power the mean variation and using the result as a figure of merit. Price will naturally act as the final determining factor.

Details of the methods of testing and tables of results are given.

"*The Determination of Sucrose (Cane Sugar) in Beet Sugar Factory Products by Clerget's Process, Using Invertase as Hydrolyst.*" By James P. Ogilvie.

In determining the percentage of sucrose in sugar factory products by the Clerget process it has been recognised for some time past that other bodies than the sucrose, such as the "gums," vegetable acids, and certain nitrogenous compounds, may be affected by the acid, the actual value which the determination is intended to express thus being vitiated. In view of this, several well known investigators have proposed the use of invertase as a hydrolyst capable of acting upon the sucrose alone in presence of impurities of the nature indicated. Ling and Baker (*Journ. Soc. Chem. Ind.*, 1898, 111) have found that the values for Clerget by invertase differed appreciably from those obtained in the ordinary way; whilst more recently Hudson (*Intern. Sugar Journ.*, 1910, xii., 192), on the contrary, concluded as the result of an examination of cane syrup and bagasse that the invertase method gives results agreeing with those found by acid. In now investigating this question with beet molasses the author shows that, contrary to what might at first sight be expected, the invertase method gives distinctly higher results, and this invariably so in each of the samples examined. With the object of explaining these higher results, attention is called to the work of Andrlik and Stanek (*Zeit. Zuckerind. Böhm.*, 1906, xxxi., 417) on the optically active non-sugar of sugar factory products. Briefly summarised, these investigations show that, owing to the rotation of the optically active amido-acids varying according to the reaction of the solution, an error exists in taking the direct reading in an alkaline solution (to basic lead acetate used for defecation) and the inversion reading in an acid solution (to the hydrochloric acid used for inversion). If instead of taking the direct reading in a solution alkaline to basic lead acetate it is read in a solution of the same acid concentration (urea being added to inhibit inversion), as the inversion reading appreciably higher results are obtained, and Andrlik and Stanek contend (*loc. cit.*) that this method of direct acid polarisation is the only one giving the true sucrose value. On applying these considerations to the problem under investigation, the author found that the invertase method gives results agreeing well with those obtained by the acid method, when allowance is made for the influence of the non-sugar by the direct acid polarisation. From this it is suggested that the fact is established that invertase is, so far as beet molasses is concerned, a selective hydrolyst, acting only upon the sucrose present, and not modifying the rotatory power of the non-sugar. The author, however, does not advocate the invertase method as a practical process. He shows that the influence of

the optically active non-sugar may also be overcome by taking the direct polarisation in a solution acid to sulphurous acid in the manner first recommended by Pellet (*Bull. Assoc. Chim. Sucr. et Dist.*, 1891, ix., 439, 624), and this method is now recommended as being preferable to the Andrlik and Stanek procedure on account of ease of manipulation and several other apparent reasons.

RÖNTGEN SOCIETY.

Prof. Ernest Rutherford, of Manchester University, read an important paper at the meeting of the Röntgen Society on January 5th, his subject being the Radio-activity of Thorium.

It was largely a *résumé* of the work which has been done by Otto Hahn on the Continent, and by Rutherford and Soddy in this country, upon the radio-active products of this substance. He examined first the products of the emanation or ratio-active gas which diffused out of the thorium compound. This gas, he said, produced an excited activity upon substances which were exposed to its presence, and it broke up at a definite rate, one-half disappearing in fifty-four seconds, one-half of the remainder in the next fifty-four, and so on, until in ten minutes it disappeared. But thorium emanation gave rise to an active deposit which analysis showed to consist of four substances. In the first place, an α-particle—really a charged atom of helium—was expelled, and we had the first of the active deposits, which was called Thorium A. This substance, although the longest-lived of the four, was not permanent, and decayed to half value in 10·6 hours, its periodicity governing the rate of final disappearance of the active deposit as a whole. Following the emission of an α-particle, which accompanied the transformation of one radio-active substance into another, they had in succession Thorium B, Thorium C, and Thorium D, which last emitted β- and γ-rays. Although the activity of a plate covered with this active deposit would disappear within a few days, falling to half value in 10·6 hours, an exceedingly active plate, even though the activity only lasted for a day or two, would have a great deal of possible utility. The activity of radium under like circumstances practically disappeared in two or three hours. Thorium remained fully active for as many days.

Turning to the substances derived from the transformation of thorium itself and not its emanation, Prof. Rutherford began with Thorium X. It was mainly from the work upon this substance that the general theory of disintegration was put forward. It was easily separated from thorium; the latter was precipitated by ammonia, and Thorium X, containing only a trace of thorium itself, was left in the solution. It fell to half value in 3·6 days, and disappeared within a month from its separation. Hahn's discovery that there must be another substance present in addition to Thorium X was the next step. To this substance was given the name of Radio-thorium, and it declined to half value in two years. Finally, the attempt to separate Radio-thorium directly from thorium led to the discovery of yet another intermediate substance between the two, namely, meso-thorium, having a half period of 5·5 years. This meso-thorium had almost exactly the same chemical properties as Thorium X, and although, as stated, if isolated from its spontaneously appearing family of products its half period was 5·5 years, it would in the course of a few years "grow" radio-thorium and begin another cycle of changes. It emitted β- and γ-rays, like Thorium D of the active deposit of thorium emanation, and although initially it had no α-radiation the radio-thorium into which it grew emitted α rays. Altogether, the activity of meso-thorium would rise for about 3·5 years after separation, when it would be twice as great as it was at the beginning. It would then die away with time, but even after ten years its activity would be higher than when the original meso-thorium was separated.

As thorium was used in large quantities commercially the extraction of meso-thorium could be made the more conveniently, especially as the active substances could be separated without injuring the main product. For medical purposes the substance was equally as good as radium, having β-rays of about the same penetrating power, and γ-rays perhaps of slightly greater penetrability. It could and would be produced in quantity, and although the labour of extraction was greater than that involved in the extraction of radium, the fact that thorium was wanted commercially made it more than possible that very large quantities of these active substances would be produced, and he anticipated that the price would be much smaller than the present price of radium, which was quite fantastic.

NOTICES OF BOOKS.

Outlines of Experimental Chemistry. By Ernest Bowman Ludlam, D.Sc. (Liverpool), F.C.S., and Haydn Preston, A.R.C.Sc. (London). London: Edward Arnold. 1910.

This book is described by its authors as a compromise between the old-fashioned method of teaching practical chemistry, which included nothing but qualitative analysis and perhaps a little elementary gravimetric work, and the modern heuristic method. According to the old plan very little scope was given to the student's initiative and reasoning power, and all he was required to do was to follow explicit directions, and to make the observations he was told to expect. However great an advance the modern method may represent, and excellent as may be the results obtained by it in favourable circumstances, it has for some time been recognised as by no means ideal, and the fusing of the merits of the two is the problem now before the teacher of science. This problem the authors have attacked with confidence, and, moreover, with a large measure of success. Their scheme is systematic, and minimises the organising work of the teacher. The course is adapted for young students doing quite elementary work, and continues to fairly advanced gravimetric and volumetric analysis and some elementary physical chemistry; in fact, the range of subjects is rather wide, and a more detailed study of some branches would perhaps provide better training. The directions are occasionally somewhat lacking in clearness, owing partly to their extreme brevity, but the authors' intention is obviously not to do away with the need for a teacher, and the book should certainly stimulate thought and arouse interest.

The Science of Poetry and the Philosophy of Language. By Hudson Maxim. New York and London: Funk and Wagnalls Co. 1910.

The author of this book suffers from no lack of courage, and his attitude towards even the giants of the poetical world is one of undaunted criticism. Briefly, he believes that all phenomena can profitably be made the subject of scientific research. Granted then that poetry is a phenomenon, its origin and structure can, by analytical study, be so far elucidated that its synthesis becomes a mere rule-of-thumb process, and the would-be poet has only to follow the rules, when his success is certain. This central idea is worked out with the utmost temerity. Distinction is drawn between poetry and verse; serious discussion of what is and what is not the former fills many pages of the volume, and finally the author boldly challenges the criticism of his readers by paraphrasing Milton and Shakespeare, and suggesting improvements upon their phraseology. At the end of the book he gives a collection of about 150 specimens of true poetry, some written by himself, following his own rules, some by the poets who have been called greater, and some by others who, according

to usual ideas, are of lesser excellence, and a very amusing half-hour could be spent ascertaining with the help of the key the authorship of the less well-known examples. The book is to say the least, a bold attempt to introduce scientific method into a subject which has hitherto been regarded as above and beyond the scope of the processes of the scientific investigator, and at any rate its readers will find in it a cure for boredom, wherever they may open it.

Practical Physiological Chemistry. By R. H. Aders Plimmer, D.Sc. London, New York, Bombay, and Calcutta: Longsmans, Green, and Co. 1910.

In this book is given a very full course of practical physiological chemistry, by means of which a thorough training in the laboratory methods employed could be obtained, and after working through it the student would be able to proceed straight to research work in the subject. The plan of the book seems excellent. On the subject of each section some notes are given, outlining the essential points and giving a summary of the knowledge which it is necessary for the student to have in order that he may understand the full significance of the practical work. These explanatory notes are well chosen and of exactly the right length for their purpose, and the author has shown much skill in selecting the important features and summarising them in the most lucid way. The practical work on each subject then follows, and full directions are given for the carrying out of a large number of experiments, beginning with the study of the more important organic compounds and passing on to special physiological methods and to the investigation of biological processes and products.

The Aynsome Annual, 1910. Edited by J. Stewart Rimington, F.C.S. Frome and London: Printed by Butler and Tanner.

This annual contains a collection of articles and papers which have been written by the Director of the Aynsome Technical Laboratories and his assistants during 1909. The papers, which have been reprinted from the *World's Paper Trade Review*, the *Oil and Colour Trades Journal*, &c., deal with the examination of various fibres, in order to test the possibility of profitably using them for paper-making, the analysis of some technical products such as litharge, and the analysis of cereals and cereal foods.

A Text-book of Organic Chemistry. By William A. Noyes. Second Edition. New York: Henry Holt and Co. 1910.

The treatment of the compounds of carbon given in this book follows the conventional lines except that the fatty and aromatic derivatives are not separated. It is evidently intended for beginners, who, however, are capable of profiting by fairly difficult discussions, and the number of substances described is extremely though perhaps unavoidably large. The aim of the author, however, has evidently been to lighten the burden on the student's memory as far as possible, and the summaries of general methods of preparation and characteristic properties of groups of substances are a valuable feature. Some notes and hints are given on suitable practical work to be performed in conjunction with the study of the book. Possibly for beginners, even if they are not very young, the book is rather overloaded with detail, and it hardly seems an ideal plan to describe fully all the hydrocarbons, for instance, before attacking any other group of compounds. In the new edition the method of classifying the proteins of the American Society of Biological Chemists and the American Physiological Society is adopted, and the chapter on Compounds of Interest in Physiology and Pathology has been re-written, while the changes and additions which were made for the German edition of the book have also been included in it.

Die Aetherischen Oele. By Dr. Robert Leimbach. Halle-a-S.: Wilhelm Knapp. 1910.

The treatment of the ethereal oils in this book is sufficiently full for all the purposes of the analytical chemist and manufacturer. In the earlier chapters the development of the ethereal oil industry is discussed, and descriptions are given of the methods of extraction of the more important representatives of the class and of the physical and chemical methods of investigating them. The detection of the constituents of the ethereal oils is next treated in detail, and the second half of the book gives, in tabular form, a complete summary of all the known oils, their origin, methods of distillation, percentage yield, physical constants, special distinguishing characteristics and constituents, as far as they have been identified. In addition a valuable bibliography is given for each oil, and further notes are in some cases added upon their probable impurities, world's production, and history.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 20, November 14, 1910.

Tempering of Bronzes.—L. Grenet.—Theoretically annealing after tempering ought to bring bronze into the same state as if it had been slowly cooled, and, as the transformation would take place at a lower temperature, the metal after tempering and slight annealing would be harder than the metal when annealed at a higher temperature. Experiments with two different bronzes containing 85 and 80 per cent of copper respectively confirmed these conclusions.

Double Sulphates formed by Sulphates of Lanthanum and Cerium with Alkaline Sulphates.—M. Barre.—Solubility curves indicate the formation of the following double compounds:—

$La_2(SO_4)_3.K_2SO_4.2H_2O$,	$Ce_2(SO_4)_3.K_2SO_4.2H_2O$,
$La_2(SO_4)_3.5K_2SO_4$,	$2Ce_2(SO_4)_3.3K_2SO_4.8H_2O$,
$La_2(SO_4)_3Na_2SO_4.2H_2O$,	$Ce_2(SO_4)_3.5K_2SO_4$,
$La_2(SO_4)_3.(NH_4)_2SO_4.2H_2O$,	$Ce_2(SO_4)_3.Na_2SO_4.2H_2O$,
$2La_2(SO_4)_3.5(NH_4)SO_4$,	$Ce_2(SO_4)_3(NH_4)_2SO_4.8H_2O$,
$La_2(SO_4)_3.5(NH_4)_2SO_4$,	$Ce_2(SO_4)_3.5(NH_4)_2SO_4$.

It is noticeable that ammonium sulphate like the sulphates of potassium and sodium diminishes the solubility of the sulphates of cerium and lanthanum. Thus their solubility in solutions of ammonium sulphate is greater than in solutions of sodium sulphate or potassium sulphate, but much ower than the solubility in pure water.

Reduction of Phosphorus Oxychloride by Hydrogen under the Action of the Electric Discharge.—A. Besson and L. Fournier.—When a mixture of vapour of $POCl_3$ and pure dry hydrogen is passed through a silent discharge tube a yellow solid appears on the poles. The composition of this substance is represented by the formula P_2O, and the equation is $2POCl_3 + 8H = P_2O + 6HCl + H_2O$. The small quantity of water formed reacts with the excess of $POCl_3$, giving pyro- and meta-phosphoric oxychlorides.

Action of Pyridine on Iridodisulphates.—Marcel Delépine.—A solution of pyridine reacts very slowly at the ordinary temperature, and more rapidly on heating on a solution of an iridodisulphate, giving salts of a pyridino-iridodisulphuric acid, $\left[Ir\begin{matrix}(C_5H_5N)OH\\SO_4-\\SO_4-\end{matrix}\right]H$, derived from the iridodisulphuric acid, $\left[Ir\begin{matrix}(H_2O)OH\\SO_4-\\SO_4-\end{matrix}\right]H$, by the sub-

stitution of pyridine for the intramolecular water. The author has prepared and analysed the following salts:— $P''(NH_4)_1{\cdot}5H_2O{\cdot}5.H_2O$, $P''Na_3H_4{\cdot}1{\cdot}5H_2O$, $P''K_4H_2{\cdot}2H_2O$, $P''Ba_3H_2{\cdot}3H_2O$, $P''Ag_4H_4{\cdot}H_2O$, in which "P" stands for the radicle $|HO(C_5H_5N).Ir(SO_4)_2|''$. They are all green salts, more or less soluble in water and insoluble in alcohol and ether. They are stable in the solid state and in neutral solution, but are attacked by strong acids and alkalis, especially on heating.

Gases occluded in Copper Alloys.—G. Guillemin and B. Delachanal.—Brass retains in the occluded state a considerable volume of gas (1—30 volumes), composed chiefly of hydrogen, carbon dioxide, and carbon monoxide. Phosphor bronzes retain but little occluded gas, composed of carbon dioxide and hydrogen. Commercial tin contains small quantities of carbon dioxide, hydrogen, and carbon monoxide.

New Method of preparing Glycidic Ethers.—G. Darzens.—Ethyl dichloracetate condenses with acetone in presence of magnesium amalgam as follows:—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO + Cl{-}CHCl\quad CO_2C_2H_5 + Mg \rightarrow$$

$$\rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}OMgCl\\CHCl{-}CO_2C_2H_5.\end{matrix}$$

With water and acetic acid the solution yields α-chlor-β-oxyisovalerianic ether of formula—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C(OH){-}CHCl\quad CO_2C_2H_5.$$

From this ether, dimethyl glycidic ether can be obtained by treatment with the theoretical amount of sodium ethylate. This last reaction is important because it is general and enables a large number of glycidic ethers to be prepared, starting with an α-β-ethylenic acid.

Constitution of Vicianose and Vicianine.—Gabriel Bertrand and G. Weisweiller.—From the results of the oxidation of vicianose it appears that the glucose and arabinose entering into its composition are united by the aldehydic function of the pentose, and if it is assumed that the mode of linking is oxidic (as is most probably the case) the composition of the new saccharide can be represented by the formula—

$$CH_2OH{-}(CH.OH)_2{-}CH{-}CH{-}O{-}CH_2{-}$$
$$\diagdown\ \diagup$$
$$O$$
$$-(CH.OH)_3{-}CH.OH{-}COH.$$

Vicianine would then have the formula—

$$CH_2{-}OH(CH.OH)_2{-}CH{-}CH{-}O{-}CH_2(CH.OH)_3{-}$$
$$\diagdown\ \diagup$$
$$O$$
$$-CH{-}CH{-}O{-}CH{-}C_6H_5$$
$$\diagdown\ \diagup\qquad\quad|$$
$$O\qquad\quad CN$$

No. 21, November 21, 1910.

Progressive Phosphorescence Spectra of Organic Compounds at Low Temperatures.—J. de Kowalski and J. de Dzierzbicki.—The authors have examined the progressive phosphorescence of a series of hydrocarbons of the aromatic series and other benzene derivatives, and have found that this property depends essentially upon the constitution of the substance under examination.

Propiolic Compounds. Cyanacetylene.—Ch. Moureu and J. Ch. Bongrand.—Cyanacetylene, $HC{\equiv}C{-}CN$, can be prepared by dehydrating propiolamide, $HC{\equiv}C{-}CONH_2$, which is obtained by the action of ammonia on propiolic methyl ester, $HC{\equiv}C{-}CO_2CH_3$, at a temperature below 0°. Cyanacetylene is a mobile liquid with a strong irritating odour. It is very inflammable. It is slightly soluble in water and readily soluble in alcohol. Its boiling-point is 42·5, and it solidifies at + 5°. Density = 0·8159. Cyanacetylene is interesting because organic compounds, which have only one atom of hydrogen in the molecule, are very rare. The copper salt of cyanacetylene, $Cu_2(C_3N)_2$, when oxidised with potassium ferricyanide ought to give the compound C_6H_2. It has been found that thus small quantities or fine white needles fusible at 64° can be obtained. They are very volatile and unstable, and resemble C_4N_2 in smell and in their irritant properties, and probably they are the substance C_6N_2.

No. 22, November 28, 1910.

Nitration of Mono- and Di-acetylated Aromatic Amines.—Frédéric Reverdin and Armand de Luc.—Di-acetylated derivatives are nitrated only at a higher temperature than that necessary for the nitration of the mono-acetylated derivatives. The presence of two acetyl groups in the molecule of *p*-toluidine diminishes the stability of the compound.

Glucodeconic Acids.—L. H. Philippe.—The author has synthesised α-deconic amide, $C_{10}H_{21}O_{10}N$, by the usual method, and also β-deconic lactone from which the acid anhydride,—

$CH_2OH{-}(CH.OH)_8{-}CO{-}O{-}CO{-}(CH.OH)_8{-}CH_2OH$,

can be obtained by concentrating the solution.

MEETINGS FOR THE WEEK.

Tuesday, 17th.—Royal Institution, 3. "Heredity," by Prof. F. W. Mott, F.R.S., &c.

Wednesday, 18th.—Royal Society of Arts, 8. "The Dutch Labour Colonies" by J. C. Medd.

—— Microscopical, 8. Annual Address of the President, Prof. J. Arthur Thomson, M.A.

Thursday, 19th.—Royal Society of Arts, 4.30. "Banking in India," by Reginald Murray.

—— Chemical, 8.30. "Intramolecular Rearrangement of Diphenylmethane ω-Sulphoxide," by T. P. Hilditch and S. Smiles. "Reactions between Chemical Compounds and Living Muscle Proteins," by V. H. Veley. "Interaction of Alloxan and Glycine," by W. H. Hurtley and W. O. Wootton. "Decomposition Products of Tetramethylammonium Nitrite under the Action of Heat," by P. C. Rây and H. K. Sen. "Retardation and Acceleration in the Dissolution of Mercury in Nitric Acid in presence of Minute Quantities of Ferric Salts and Manganese Nitrate," by P. C. Rây. "On *al*- and *d*-Δ²-*m*-Menthenol(8) and *dl*- and *d*-Δ²:8(9)-*m*-Menthadiene," by W. N. Haworth, W. H. Perkin, and O. Wallach. "Identity of Xanthaline with Papaveraldine," by Miss B. Dobson and W. H. Perkin. "Amalgams containing Silver and Tin," by R. A. Joyner. Studies of the Constitution of Soap in Solution—the Electrical Conductivity of Sodium Stearate Solutions," by R. C. Bowden. "Additive Compounds of Phenols and Phenolic Ethers with Polynitro-aromatic Derivatives," by J. J. Sudborough and S. H. Beard. "Effect of Contiguous Unsaturated Groups upon Optical Activity—Part VI., Influence of the Carbonyl Group upon Optical Rotatory Power—Part VII., Relative Influences of Aromatic and Hydroaromatic Nuclei upon Optical Rotatory Power—Part VIII., Influence upon Optical Activity of Two Contiguous Unsaturated Groups in Comparison with that of One Unsaturated Group at varying Distances from the Optically Active Complex" and "The Relative Effects of Ethylenic and Acetylenic Linkings upon Optical Rotatory Power," by T. P. Hilditch. "Direct Action of Radium on Ammonia," by E. P. Perman. "Cuprittartrates and Analogous Compounds," by S. U. Pickering.

—— Royal Society. "Action of *B. lactic aerogenes* on Glucose and Mannitol," by G. S. Walpole. "The Pharmacological Action of South African Boxwood (Gonioma Kamassi)," by Dr. W. E. Dixon. "Autoagglutination of Red Blood Cells in Trypanosomiasis," by Dr. W. Yorke. "Transformation of Proteids into Fats during the Ripening of Cheese," by M. Nierenstein. "The Action of X-rays on the Developing Chick," by J. F. Gaskell.

—— Royal Institution, 3. "Recent Progress in Astronomy," by F. W. Dyson, Astronomer Royal.

Friday, 20th.—Royal Institution, 9. "Chemical and Physical Change at Low Temperatures," by Prof. Sir James Dewar, F.R.S., &c.

Saturday, 21st.—Royal Institution, 3. "Problems in the Career of the Great Napoleon," by Arthur Hassall, M.A.

THE CHEMICAL NEWS.

VOL. CIII., No. 2669.

NOTE ON THE TEMPERATURE SCALE BETWEEN 100° AND 500° C.*

By C. W. WAIDNER and G. K. BURGESS.

AT the present time the standard scale of temperatures in the interval 0° to 100° C. is that defined in a resolution of the International Committee on Weights and Measures, namely, that of the constant volume hydrogen thermometer (1).† Above 100° temperature measurements have been made with air, hydrogen, and nitrogen thermometers, and in recent years there seems to be a preference to work with the constant volume nitrogen thermometer.

In a previous paper (2) the authors determined the melting- and freezing-points of a number of metals on the temperature scale defined by the platinum resistance thermometer calibrated in ice, steam, and sulphur vapour (444·70° on the constant volume nitrogen thermometer). In order to throw further light on the probable accuracy of the temperature scale so defined, in the interval 100° to 500° C., the authors have made some further measurements by the same method on the boiling-points of naphthaline and benzophenone, which temperatures have been determined by a number of observers using both platinum and gas thermometers.

Four thermometers were used, made of different sizes of pure platinum wire from Heraeus, and from Johnson, Matthey, and Co., and having fundamental intervals ranging from 1·1 to 10·6 ohms. Three of these thermometers were used both as Siemens three-lead compensated, and as four-lead potential terminal thermometers. The apparatus and methods are fully described in the previous paper.

The boiling-points were determined with the sulphur-boiling apparatus, using glass tubes about 4·5 cm. diameter and 45 cm. long, furnished with a side condenser tube with inlet near the top, and the thermometer was shielded by an aluminium cone in exactly the same way as in sulphur. With this shield omitted, the thermometer readings were about 0·08° low in naphthaline and 0·35° low in benzophenone. Raising the thermometer 6 cm. produced a lowering in temperature of less than 0·02°.

Besides the boiling-point determinations, a few measurements were also taken of the freezing-points of tin, cadmium, and zinc to compare with the previous work. The results are given in Tables I. and II. It will be seen that the freezing-points newly determined are practically identical with those previously found by the authors, showing that the temperature scale of the present work is in agreement with that of the previous investigation.

The reduction of the boiling-points to normal pressure was made by means of formulæ satisfying the data both of Crafts and of Jaquerod and Wassmer.

For naphthaline : $-T_{760} = T_{obs.} - 0{\cdot}058\ (H - 760)$.
For benzophenone : $-T_{760} = T_{obs.} - 0{\cdot}063\ (H - 760)$.

The freezing-points of 250-grm. samples of the naphthaline and benzophenone used were found to be as follows :—

Description.	Freezing-point of—	
	Benzophenone.	Naphthaline.
From Kahlbaum	47·2	79·9
From Kahlbaum, re-crystallised ..	47·2	80·4
From Merck, re-crystallised.. ..	46·9	—

* *Bulletin of the Bureau of Standards*, vol. vii., No. 1, Washington, 1910.

† References will be found at the end of the paper

In Table III. are collected the determinations of the boiling-points of naphthaline and benzophenone as made by the various observers, and where possible the values have been reduced to the same basis, namely, to a scale on which the sulphur boiling-point is 444·70°.

It will be seen that, with the exception of the determinations of Jaquerod and Wassmer, there is a close agreement. Their results may be low, owing to the fact that the condenser of their boiling apparatus was immediately above the gas thermometer bulb, which was not screened in any way against the cooling effects of condensation and radiation. It should also be noted that the volume of their gas thermometer bulb was only 66 cc., which is small for work of precision. Their results may be indirectly tested by assuming either of their boiling-points as the third standardisation temperature of a platinum thermometer, and using the therometer so calibrated to determine the sulphur boiling-point. This procedure would give S b.p. = 443·0°, a value 1·5° lower than any determination, and for the constant δ of the platinum thermometer 1·40 instead of the usual 1·50 as found when S b.p. = 444·7 is used as the third standardisation temperature.

In view of the very general use of the S b p. for the standardisation of platinum thermometers, we have summarised in Table IV. the results of the more important determinations of this temperature, and reduced them to the same basis, namely, that of the nitrogen constant volume thermometer under a pressure of 1 metre of Hg at 0° C. The temperatures thus observed are obtained only under very definite experimental conditions, which are described at length in the previous paper and elsewhere.

Messrs. Day and Sosman in a recent elaborate investigation (15) with a nitrogen constant volume thermometer at high temperatures (400° to 1550° C.) have determined the freezing-points of a number of metals, among them zinc and cadmium, by transferring from the gas scale with thermo-couples. They find for the freezing-point of zinc 418·2°, and for cadmium 320·0°, whereas the platinum resistance thermometer calibrated in ice, steam, and sulphur vapour (444·70°) gives 419·4° and 321·0° for zinc and cadmium respectively, with a precision of 0·05° C. The explanation of this difference is of great importance in accurately fixing the gas scale in the interval 100° to 500° C. If the freezing-point of pure zinc is 418·2°, instead of 419·4°, then it would follow that the boiling-point of sulphur must be 443·5° instead of 444·7°, as found by a number of observers as shown (see Table IV.).

It should also be noted that the gas thermometer as used by Day and Sosman was adapted primarily to give the highest attainable accuracy for the higher range of temperatures—that is, above 1000° C., and that no measurements with the gas thermometer itself were made below 400°, nor did they consider their thermometer of sufficient sensitiveness in the lower temperature ranges to warrant a determination of its fundamental interval, 0—100° C.

Some further evidence on the accuracy of the gas scale that is defined by a platinum resistance thermometer calibrated in ice, steam, and sulphur (444·70°) is afforded by the comparison by Holborn and Henning of two platinum thermometers with a nitrogen thermometer in the interval 150° to 200° C. This work shows that the two scales so defined are in agreement to within a few hundredths of a degree. If the value usually assigned to the S b.p. (444·70°) were over 1° high, then the scale defined by the platinum thermometer at 200° might be expected to be about 0·2° high, whereas these observers find an extraordinarily close agreement between these two scales. It is also of interest to note that these observers give evidence that their gas thermometer agrees with Regnault's gas scale to within 0·02° up to 230° C.

In view of the doubt, however, which is thrown on the present generally accepted value of the S b.p. by the work of Day and Sosman, new determinations of this point made with the best modern facilities with apparatus designed for work in this range are much to be desired.

TABLE I.

Determinations of Boiling-points of Naphthaline and Benzophenone. Wheatstone Bridge and Potentiometer Methods.

On Ice, Steam, Sulphur (=444·70) Scale of Platinum Resistance Thermometer.

Date. 1910.	Therm. No.	Method.	Observed resistance.	R_0.	F.I.	δ.	Observed Pt temp. Pt_{ft}.	Observed temp. of boiling.	Reduced barometer.	Boiling-point.	Substance.
				1. *Boiling-point of Naphthaline.*							
3 29	1787 B	W.B.	20·8987	11·5263	4·3787	1·513	214·04	217·93	758·34	218·03	K
3 30	,,	,,	20·8953	11·5263	4·3787	1·513	213·97	217·85	756·74	218·04	K
4·19	,,	,,	20·8572	11·5202	4·3784	1·513	213·11	216·95	742·11	217·99	K 1 recrys.
3 29	1787 C	,,	6 33964	3·17222	1 33965	1 505	214·04	217·91	757·99	218 03	K
3 30	,,	,,	6 33815	3·47222	1·33965	1 505	213·93	217 79	756·54	217·99	K
4·19	,,	,,	6·32746	3·47219	1·33975	1·505	213·12	216·94	742·03	217·98	K 1 recrys.
3 29	1787 D	,,	51·6262	28·7925	10 6674	1·500	214·05	217·90	757 98	218 02	K
4·15	,,	,,	51·5562	28·7923	10·6674	1·500	213·40	217·22	747·06	217 97	K 1 recrys.
4·19	,,	,,	51 5307	28·7921	10·6675	1·500	213 16	216 97	742 49	217 99	K ,,
4·28	,,	P.T.	52 5706	28·7801	10·6623	1·500	213·75	217·59	753·15	217·99	K ,,
4·15	1787 F	W.B.	5·27421	2·89055	1·11702	1·502	213·39	217·21	746 89	217·97	K ,,
4·19	,,	,,	5·27122	2·89055	1·11702	1·502	213·13	216·94	742·33	217·97	K ,,
4·28	,,	P.T.	5·32087	2·93016	1·11854	1·500	213 73	217·57	752 85	217 98	K ,,
4·28	,,	,,	5·32080	2·93016	1·11854	1·500	213·73	217·57	752·94	217 98	K ,,
				Boiling-point of naphthaline, Kahlbaum						218·02 ± 0·01₄	
				Boiling-point of naphthaline, Kahlbaum, 1 recrys.						217·98 ± 0·01₁	
				2. *Boiling-point of Benzophenone.*							
4 6	1787 B	W.B	24·4616	11·5263	4·3787	1·513	295·41	304·85	741·14	306·04	K
4·8	,,	,,	24 4884	11·5263	4·3787	1·513	296·03	305·53	751·20	306·08	K
4·14	,,	,,	24·4989	11·5263	4·3785	1·513	296·27	305·79	752·31	306·27	M 2 recrys.
5·3	,,	P. T.	24·4585	11·50955	4·3739	1·511	295·05	305·54	751·86	306·05	K recrys.
4 6	1787 C	W.B.	7·42996	3·47222	1·33965	1·505	295·43	304·83	742·01	306·02	K
4·8	,,	,,	7·43603	3·47222	1·33965	1·505	295·89	305·32	751·99	305·83	K
4·8	1787 D	,,	60·3668	28·7925	10·6674	1·500	295·99	305·40	750·83	305·98	K
4·8	,,	,,	60·3716	28·7925	10·6674	1·500	296·03	305·43	750·81	306·02	K
4·14	,,	,,	60·3943	28·7925	10·6674	1·500	296·25	305·68	752·58	306·15	M 2 recrys.
4·8	1787 F	,,	6 19652	2·89056	1·11703	1·502	295·96	305·38	750·92	305·95	K
4·14	,,	,,	6·19967	2·89056	1·11703	1·502	296·24	305·68	252·15	306·17	M 2 recrys.
5·3	,,	P.T.	6 24232	2·93016	1·11854	1·500	296·11	305·53	752·11	306·03	K recrys.
				Boiling-point of benzophenone, Kahlbaum						306·00 ± 0·053	
				Boiling-point of benzophenone, Merck, 2 recrys.						306·2	

Some measurements made in 1907 by one of the authors also gave for Kahlbaum naphthaline boiling-point 218·02°.

TABLE II.—*Freezing-points of Tin, Cadmium, and Zinc.*

(To connect with Temperature Scale of previous Investigations).

Date. 1910.	Therm. No.	Method.	Observed resistance.	R_0.	F.I.	δ.	Pt.	Freezing-point.	Remarks.
			1. *Freezing-point of Tin.*						
4·2	1787 F	W.B.	5·42965	2·89056	1·11703	1·502	227·31	231·91	K in Acheson graphite.
4·27	,,	P.T.	5·47290	2·93016	1·11854	1·500	227·32	231·91	,, ,,
4·27	1787 D	,,	53·0111	28·7801	10 6623	1·500	227 25	231·84	,, ,,
			Range of previous observations (five samples) ..					(231·94) (231·83)	K gave 231·92.
			2. *Freezing-point of Cadmium.*						
4·1	1787 C	W.B	7·63076	3·47222	1·33965	1·505	310·42	321·10	K in Acheson graphite.
4 1	1787 D	,,	61·9000	28·7925	10·6674	1·500	310·36	321·00	,, ,,
4·1	1787 F	,,	6·35755	2·89056	1·11703	1·502	310·38	321·03	,, ,,
			Range of previous observations (three samples)..					(321·05) (320·39)	K gave 321·01.
			3. *Freezing-point of Zinc.*						
4·28	1787 D	P.T.	71·3483	28·7801	10 6623	1·500	399·24	419·32	K in Dixon graphite, 1907 crucible.
			Range of previous observations (five samples) ..					(419·46) (419·25)	K (three samples) gave 419 37.

K = Kahlbaum best grade, M = Merck, W.B. = Wheatstone bridge with Siemens three lead thermometer, P.T = potential terminal thermometer, R_0 = resistance in ice, F.I. = fundamental interval, δ = constant in the formula $t-pt=\delta(t/100-1)t/100$.

Table III.—*Boiling-points of Naphthaline and Benzophenone.*

Date.	Observers.	Method and Remarks.	Naphthaline. Observed.	Naphthaline. Reduced to S.B.P.= 444·70.	Benzophenone. Observed.	Benzophenone. Reduced to S.B.P.= 444·70.
1883	Crafts (3)	Hydrogen thermometer	218·06	218·03	306·08	306·01
1891	Callendar and Griffiths (4).	Pt thermometer compared with c.p. air thermometer (S.B.P. = 444·53) ..	217·94	217·97	305·82	305·89
1891	Griffiths (5)..	Do.	218·04	218·07	—	—
1904	Jaquerod and Wassmer (6)	Hydrogen thermometer	217·68	(217·65)	305·44	(305·37)
1905	Travers and Gwyer (7) ..	Platinum thermometer (S.B.P. = 444·53)	218·04	218·07	305·8	305·87
1908	Holborn and Henning (8) .	Pt thermometer compared with c.v. nitrogen therm. (S.P.B. = 445·00) .	218·04	217·99	306·08	305·95
1910	Waidner and Burgess ..	Platinum thermometer (S.B.P. = 444·70)	—	217·98	—	306·02
		Reduced mean, including all observations..	217·97 ± 0·08		305·85 ± 0·16	
		Reduced mean, excluding Jaquerod and Wassmer	218·02 ± 0·04		305·95 ± 0·05	

Table IV.—*Boiling-point of Sulphur by Gas Thermometer.*

Date.	Observer.	Method and remarks.	Observed S.B.P.	Reduced to const. vol. p_0=1 m. Hg.	Weight.
1862	Regnault (9)	Constant volume ; by interpolation	447·5	—	—
1891	Callendar and Griffiths (4)	Constant pressure	444·53	444·74	2
1894	P. T. Reichsanstalt (10)..	Constant volume ; Wiebe and Bötcher scale ..	444·5	444·5	1
1900	Chappuis and Harker (11)	Constant volume, corrected from 445·2..	444·7	444·7	2
1901	Holborn (12)	Constant volume, extrapolated by Pt resistance..	444·55	444·55	1
1903	Rothe (13)..	Constant volume P.T.R. scale, Hg thermometers (Thermocouples gave 445·0).	444·7	444·7	1
1909	Eumorfopoulos (14).. ..	Constant pressure .. .. (Extrapolated for Hg expansion = 443·7).	444·55	444·76	2
		Mean S.B.P.	444·68 ± 0·08		

Ordinarily one would conclude that the highly satisfactory agreement of the determinations by so many different observers, using different methods, as summarised in Table IV., would settle this point. A careful study of the gas thermometers and methods used, however, shows that they are open to many criticisms, and many refinements are now possible that were not available or whose importance was not so clearly recognised at the time these determinations were carried out. Thus, in some of these determinations air was used as the gas instead of nitrogen. Glass or porcelain bulbs, so subject to changes in volume or to the emission or absorption of gases, were employed instead of metal bulbs. The coefficient of expansion of the bulb was not always determined with sufficient accuracy over the whole of the temperature range, and in some cases the coefficient used was found by an unwarranted extrapolation.

The use of a uniform scale by different experimenters is always most desirable. In view of the very general use of the value 444·7° as the boiling-point of sulphur on the scale of the constant volume gas thermometer, and in the light of the evidence that is now available, no change in this point is possible at this time, It is well to bear in mind, however, that the standard gas scale is not yet definitely and certainly fixed to an accuracy of 1° at 450° C.

The following table of fixed points represents the temperature scale which appears to best satisfy the available observations to 0·1° for the reproduction of temperatures in the interval 100° to 500° C. :—

Freezing-points.		Boiling-points.	
Tin	231·9° C.	Naphthaline ..	218·0° C.
Cadmium	321·0° C.	Benzophenone .	306·0° C.
Zinc . ..	419·4° C.	Sulphur	444·7° C.

As these temperatures are on the constant volume scale, the reduction to the thermodynamic scale may be effected approximately if desired by adding 0·2° at the sulphur point and a proportional amount at the lower temperatures, remembering that this correction is zero at 100° C. All of these substances may readily be obtained of sufficient purity to give a reproducibility of 0·05° C. from one sample to another.

References.

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METHODS OF ANALYSIS FOR ENAMEL.*

By ROBERT D. LANDRUM.

THE fact that practically nothing has been published on the above subject, and the remembrance of the many long hours spent in digging out these methods and adapting them to enamels and enamel raw materials, has led the author to put them in this form for others who might use them. While he claims little originality in the methods themselves, he does claim originality in the adaptations here given. Each and every one of these methods has been thoroughly tried out, either in the laboratory of the Columbian Enamelling and Stamping Co., at Terre Haute, Ind., or in the chemical laboratories of the University of Kansas.

The analysis of an enamel presents one of the most difficult and complicated problems with which the analyst comes in contact. An enamel is generally an insoluble silicate containing besides silica, iron, alumina, calcium, magnesium, and the alkalis, generally boron, fluorine, manganese, cobalt, antimony, and tin, and sometimes phosphorus and lead. Before attempting the quantitative analysis of any enamel a thorough qualitative analysis should be run, and this will enable one to choose a quantitative separation. One of the most important aids to a correct analysis is a thorough grinding. The sample should be ground to an almost impalpable powder, and every conceivable precaution for accuracy taken.

The analysis of a sample of enamel to be taken from a piece of ware involves an extra difficulty. The coating of enamel almost always consists of two or more layers—the lower a large ground coat, and the upper ones white or coloured enamels. For an illuminating analysis these must be separated. The author has found the following method of V. de Luyeres good for doing this (*Comptes Rendus*, viii., 480):—The surface is scratched lightly with a piece of emery cloth or a file, and a coating of gum acacia or glue is applied. The vessel is placed in an air-bath and heated. The glue on hardening generally carries with it some of the outer coat. The glue or gum is then broken off, dissolved in water, and the enamel pieces collected on a filter-paper. Some obstinate enamels require painstaking methods, such as chipping off with a chisel and separating the different coats—which always vary somewhat in colour—by picking out and sorting, using a pair of forceps. A large reading-glass will be useful in making these separations. Any iron from the vessel which may adhere to the enamel may be removed by means of a magnet after the sample is ground.

* From a Paper read at the Pittsburg meeting of the American Ceramic Society, February, 1910.—From the *Chemical Engineer*, xii., No. 5.

Analysis of an Enamel containing Fluorine.

In an enamel containing fluorine the usual methods for silicates cannot be used, as silicon-tetrafluoride would be volatilised in the evaporation with hydrochloric acid for the separation of the silica.

Fluorine.—One grm. sample is very finely ground, slowly fused with 2 grms. each of potassium carbonate and sodium carbonate. The melt should be kept in quiet fusion over as low a flame as possible for one hour. The melt is transferred (after cooling quickly by giving the crucible a gyratory motion while held in the tongs, causing the melt to cling to the sides instead of forming a solid cake in the bottom) to a platinum dish, where it is covered with a watch-glass, and boiled vigorously with 100 cc. of water. The residue is filtered off, and is saved for the determination of the metallic oxides and the silica.

The covered solution is digested on a steam-bath for an hour with several grms. of ammonium carbonate, and on cooling more carbonate is added, and the solution is allowed to stand for twelve hours. The precipitate of silica, alumina, &c., is filtered off, washed with ammonium carbonate water, and is saved for further determinations.

The solution containing all the fluorine and traces of silica, phosphate, &c., is evaporated until gummy, then diluted with water and neutralised as follows:—Phenolphthalein is added, and nitric acid (double normal) drop by drop until solution is colourless.

The solution is boiled, and the red colour which reappears is again discharged with nitric acid, boiled again, and neutralised again until 1 cc. of acid will discharge the colour.

The last traces of silica, &c., are now removed, as recommended by F. Seemann (*Zeit. Anal. Chem.*, xliv., 343, by the addition of 20 cc. of Schaffgotsch solution. This solution is made as follows:—250 grms. of ammonium carbonate are dissolved in 180 cc. of ammonia (0·92 sp. gr.) and the solution is made up to 1 litre). To the cold solution 20 grms. of freshly precipitated mercuric oxide are added, and the solution is vigorously shaken until the mercuric oxide is dissolved.

The precipitate caused by the Schaffgotsch solution is filtered off and saved, and the solution is evaporated to dryness and the residue taken up with water.

Any phosphorus from the bone-ash used in some enamels, and chromium which may be present, are removed from this alkaline solution by adding silver nitrate in excess. Phosphate, chromate, and carbonate of silver are here thrown down, and may be determined again if desired.

The excess of silver is removed from the solution by sodium chloride, and 1 cc. double normal sodium carbonate solution is added to the filtrate, and the fluorine is precipitated by boiling with a large excess of calcium-chloride solution.

The precipitate, consisting of a mixture of calcium carbonate and fluoride, is collected on a blue ribbon filter-paper and is washed, dried, ignited at low red-heat, separated from the filter-paper, and the residue with the ash of the paper is treated with dilute acetic acid until carbon dioxide is no longer given off on heating. The liquid is then evaporated to dryness, the residue taken up with hot water (slightly acidified with acetic acid), filtered, dried, and gently ignited and weighed as CaF_2. This may be checked by heating with sulphuric acid, driving off all the excess of acid and re-weighing as $CaSO_4$. This method gives results for the amount of fluorine, checking within 0·2 per cent, but which are generally from 2 per cent to 4 per cent low.

Silica.—For the estimation of silica and the metallic oxides, first the precipitate from the Schaffgotsch mercuric oxide solution is ignited to drive off the mercuric oxide, and the silica left is weighed. The residue from the original melt, together with the precipitate obtained by ammonium carbonate (after the drying and removal from the filter-paper, whose ash is added) are then dissolved in hydrochloric acid. The solution is evaporated to dryness

and moistened with hydrochloric acid. It is diluted with water, and the silica is filtered off, weighed, and this with that previously obtained is the total silica.

Iron, Alumina, and Manganese.—The solution from the silica is raised to boiling and the iron and aluminium are precipitated as hydroxides. Then 5 cc. of bromine water is added, and the boiling continued for five minutes. The precipitate is dried on filter-paper and ignited separately from it in a weighed platinum crucible, to which the ash of the filter-paper is afterwards added. The precipitate consists of Al_2O_3, Fe_2O_3, and Mn_2O_3, and is weighed as such. It is then fused with fifteen times its weight of potassium pyrosulphate over a low flame for three hours with the crucible covered. The crucible, contents, and cover are placed in a beaker, and dilute sulphuric acid (10 : 1) is added. By warming and continued shaking of liquid complete solution may be obtained. It is then drawn through a Jones reductor to change all the iron to ferrous, and titrated with N/10 potassium permanganate solution. The iron is calculated to Fe_2O_3, and the alumina determined by difference.

If manganese is present it is determined in a separate sample in a method given later, and is subtracted from the iron in the above. In white enamels containing only a trace of iron the manganese may be determined in the solution from the pyrosulphate fusion. A freshly prepared solution of potassium ferricyanide is added to oxidise the manganese, then the solution is made alkaline with sodium hydroxide solution, and the manganese-dioxide thus formed is filtered off. The solution is then made acid, and the ferrocyanide is titrated with N/10 potassium permanganate solution (1 cc. $KMnO_4$ = 0·00435 grm. MnO).

Calcium Oxide.—The filtrate from the iron and alumina is raised to boiling, treated with boiling ammonium oxalate solution, and digested on water-bath until precipitate readily and quickly settles after being stirred. The calcium oxalate is now filtered off, and ignited wet in platinum to constant weight over a strong blast.

Magnesium Oxide.—The solution is evaporated to dryness, and the residue ignited to remove ammonium salts. The residue is treated with a few drops of hydrochloric acid and taken up with boiling water and filtered from the carbonaceous residue. To the boiling solution is added drop by drop a solution of sodium ammonium phosphate, and is allowed to cool. Half as much concentrated ammonium hydroxide is added as there is solution, and it is allowed to stand over night. The precipitate is collected on a filter, washed with 3 per cent ammonia water, dried in oven, and ignited separate from the filter. The heat is applied gently at first, and finally with the highest heat of a good Bunsen burner. It is then weighed as $Mg_2P_2O_7$: 1 grm. $Mg_2P_2O_7$ = 0·3625 grms. MgO.

The alkalis are determined by the method of J. Lawrence Smith from a grm. sample finely powdered. This method is standard and need not be given here.

Separation and Determination of Antimony, Tin, Manganese, and Cobalt in Enamel.

Decomposition.—Two grms. finely powdered sample are transferred to a platinum dish, and after moistening with a little water, pure hydrofluoric acid is added, and the whole is mixed with a platinum spatula. The dish is digested on steam-bath for five hours covered with platinum cover (a larger platinum dish may be used for cover if no other is at hand). After the decomposition is complete the solution is evaporated to dryness on steam-bath. The residue is moistened with enough dilute sulphuric acid (1 : 1) to make a thin paste, and evaporated as far as possible on a steam-bath, and then on a hot plate, all the time being covered to prevent spirting. As soon as fumes of sulphuric anhydride cease to be evolved the cover is strongly heated until fumes cease to be driven off, when it is removed. The contents are heated by bringing the dish to dull redness directly over a Bunsen burner. The sulphates thus formed are moistened with strong hydrochloric acid, a little hot water is added, and the solution boiled with repeated additions of acid and water until completely in solution. In some enamels—especially those with high melting-points—the stannic oxide remains undissolved, and a fusion of the residue with sulphur and sodium carbonate may be necessary.

Treatment with H_2S.—The solution containing at least 30 cc. double normal hydrochloric acid is transferred to a 500 cc. Erlenmeyer flask fitted with a double bored stopper. Through one of the holes a right-angled piece of glass tubing is introduced that just reaches to the lower edge of the stopper, while through another hole another right-angled glass tube is fixed so that it almost reaches the bottom of the flask.

A Kipp H_2S generator is connected to the longer tube and H_2S is passed through for half-an-hour, and the solution is let stand for another half-an-hour, after which the sulphides of antimony and tin are transferred to a filter-paper, and the solution is kept for the determination of manganese and cobalt.

Antimony and Tin.—The precipitated sulphides are dissolved in a solution of potassium polysulphide—if any lead or copper is present it will remain undissolved and may be determined separately—by pouring this successively through the filter into a 300 cc. Jena beaker, and finally washing with water containing a small amount of potassium polysulphide.

Antimony.—The antimony and tin in this solution are separated by F. W. Clark's method as modified by F. Henz (Treadwell, vol. ii., p. 188), as follows :—

To the solution in the Jena beaker 6 grms. caustic potash and 3 grms. tartaric acid are added. To this mixture twice as much 30 per cent hydrogen peroxide is added as is necessary to completely decolorise the solution, and the latter is now heated to boiling and kept there until the evolution of oxygen is over, in order to oxidise the thiosulphate formed. All of the excess of peroxide cannot be removed successfully at this point. The solution is cooled somewhat, the beaker covered with a watch-glass, and a hot solution of 15 grms. pure re-crystallised oxalic acid is cautiously added (5 grms. for 0·1 grm. of the mixed metals). This causes the evolution of considerable carbon dioxide. Now, in order to completely remove the excess of hydrogen peroxide the solution is boiled vigorously for ten minutes. The volume of the liquid should amount to from 80 to 100 cc. After this a rapid stream of hydrogen sulphide is conducted into the boiling solution, and for some time there will be no precipitation, but only a white turbidity formed. At the end of five or ten minutes the solution becomes orange coloured, and the antimony begins to precipitate, and from this point the time is taken. At the end of fifteen minutes the solution is diluted with hot water to a volume of 250 cc., at the end of another fifteen minutes the flame is removed, and ten minutes later the current of hydrogen sulphide is stopped. The precipitated antimony pentasulphide is filtered off through a Gooch crucible, which, before weighing and after drying, has been heated in a stream of carbon dioxide at 300° C. for at least one hour. The precipitate is washed twice by decantation with 1 per cent oxalic acid and twice with very dilute acetic acid before bringing it in the crucible. Both of these wash liquids should be boiling hot and saturated with hydrogen sulphide.

The crucible is heated in a current of carbon dioxide (free from air) to constant weight, and its contents weighed as Sb_2S_3.

The filtrate is evaporated to a volume of about 225 cc., transferred to a weighed unpolished platinum dish, and electrolysed at 60° to 80° C. with a current of 0·2 to 0·3 ampère (corresponding to 2 to 3 volts). For very small amounts of tin, a current of not over 0·2 ampère should be used. At the end of six hours 8 cc. of sulphuric acid (1 : 1 are added, and at the end of twenty-four hours the solution is transferred to another dish. The deposited tin ha a beautiful appearance, similar to silver.

Tin. — The plated tin is washed thoroughly with water, and the dish is dried in an air-oven at 110°, and weighed.

The solution containing the cobalt and manganese is boiled until free from H_2S. The iron is oxidised back to the ferric state by the addition of bromine water and boiling until the excess of the latter is expelled. Ten cc. double normal ammonium chloride is added, and the iron and alumina are precipitated by the addition of ammonia, and are filtered off. (The iron alumina may be determined from this precipitate if desired).

The solution still containing the manganese and cobalt is transferred to an Erlenmeyer flask fitted for passing in H_2S, as before described, and 3 cc. strong ammonia is added. H_2S is passed through for some time, and after precipitation ceases 3 cc. more of ammonia are added, and the flask is filled to the neck (300 cc. flask), is corked, and set aside for twelve hours at least. The precipitate is collected and washed on a small filter with water containing ammonium chloride and sulphide.

Manganese. — The manganese is extracted from the precipitate on the filter by pouring through it strong H_2S water acidified with one-fifth its volume hydrochloric acid (sp. gr. 1·11). This solution from the extraction is evaporated to dryness, ammonium salts are destroyed by evaporation with a few drops of sodium carbonate solution, hydrochloric acid and a drop of sulphurous acid are added to decompose excess of carbonate and to dissolve the precipitated manganese, and the latter is re-precipitated at boiling heat by sodium carbonate after evaporating off the hydrochloric acid. The manganese is weighed as Mn_3O_4 and calculated to MnO_2, in which form it is probably present in the enamel.

The residue of cobalt sulphide left after extracting the manganese is burned in a porcelain crucible, dissolved in aqua regia, and evaporated with hydrochloric acid; the platinum—and copper, if any is present—are thrown down by heating and passing in hydrogen sulphide. The filtrate from the platinum and copper is made ammoniacal, and cobalt is thrown down by hydrogen sulphide. This is filtered off and washed with water containing ammonium sulphide. This is either ignited and weighed as oxide or more accurately determined by dissolving in an ammoniacal solution of ammonium sulphate, containing 10 grms. of ammonium sulphate and 40 cc. of concentrated ammonia for each 0·3 grm. of cobalt, and electrolysing in a weighed platinum dish at room temperature with a current of 0·5 to 1·5 ampère, and an electromotive force of 2·8 to 3·3 volts. The electrolysis is finished in three hours. The circuit is broken and the liquid poured off, and the platinum dish is washed with water, then with absolute alcohol (distilled one hour), and finally with ether, allowed to dry in oven at 95° for one minute, and then weighed. The metallic cobalt is calculated as CoO, in which form it is present in the enamel.

The Determination of Boric Anhydride in Enamel.

The boron is determined in a separate sample of about 0·3 grm. This finely pulverised sample is fused with 3 grms. sodium carbonate for fifteen minutes, is taken up with 30 cc. dilute hydrochloric acid and a few drops of nitric acid. The melt is heated in a 250 cc. round bottomed flask almost to boiling, and dry precipitated calcium carbonate is added in moderate excess. The solution is boiled in the flask after it has been connected with a 6-inch worm reflux condenser. The precipitate is filtered on an 8 cm. Buchner funnel (see method of Wherry and Chapin, *Journ. Am. Chem. Soc.*, xxx., 1688, for "Determination of Boron in Silicates"), and is washed several times with hot water, taking care that the total volume of the liquid does not exceed 100 cc.

The filtrate is returned to the flask, a pinch of calcium carbonate is added, and the solution is heated to boiling to remove the free carbon dioxide. This is best done by connecting the flask to a suction-pump, and the suction is applied during boiling. The solution is cooled to ordinary temperature, filtered if the precipitate has a red colour, and four or five drops of phenolphthalein is added, and N/10 sodium hydroxide solution is run in slowly until liquid has a strongly pink colour. A grm. of mannite (or 150 cc. of neutral glycerol) is added, whereupon the pink colour will disappear. Continue to run in N/10 sodium hydroxide until end-point is reached. Add more mannite or glycerol, and if necessary more alkali, until a permanent pink colour is obtained: 1 cc. N/10 sodium hydroxide = 0·0035 grm. B_2O_3.

Lead.—The enamel for cooking utensils should never contain lead. To determine whether a cooking utensil contains lead, E. Adam gives the following simple qualitative method:—A small piece of filter-paper moistened with hydrofluoric acid is placed upon the enamel and allowed to remain for some minutes; the paper, together with any pasty mass adhering to the enamel, is then washed off into a small platinum basin, diluted with water, and tested for lead by passing H_2S through the solution.

J. Grünwald (*Oesterr. Chem. Zeit.*, viii., 46) gives another quick test for lead:—Wet small portion of surface with HNO_3 (conc.), and heat until acid is evaporated. Add several drops of water and a few drops 10 per cent potassium iodide solution, and if even a trace of lead is present yellow lead-iodide will be produced.

Determination of Phosphoric Anhydride in Enamel.

Enamels containing bone-ash to give opaqueness are analysed for P_2O_5 as follows:—

To a grm. sample of very finely pulverised enamel in a platinum crucible 1 cc. of sulphuric acid is added and the crucible is filled half full (about 10 cc. are required) with hydrofluoric acid. The crucible is heated on the water-bath until most of the solution is evaporated, and then gently on a hot plate to remove all the fluorine as silicon-tetrafluoride and as hydrofluoric acid, but no sulphuric acid fumes should evolve, as P_2O_5 is volatile. The residue is dissolved in nitric acid and taken to dryness, moistened with nitric acid, diluted with water, filtered, and washed with a very little water.

Add aqueous ammonia to the solution from above until the precipitate of calcium phosphate first produced just fails to re-dissolve, and then dissolve this by adding a few drops of nitric acid. Warm the solution to about 70° C., and add 50 cc. ammonium molybdate solution (70 grms. MoO_3 per litre). Allow the mixture to digest at 50° for twelve hours. Filter off precipitate, washing by decantation with a solution of ammonium nitrate made acid with nitric acid.

The precipitate on the filter is dissolved by pouring through it dilute ammonia solution (1 volume of 0·96 sp. gr. ammonia to 3 volumes of water).

The solution is received in the beaker containing the bulk of the precipitate, all of which is dissolved in the ammonia solution.

An excess of magnesium ammonium chloride ("magnesia mixture") solution is added very slowly and with constant stirring. Let solution stand over night. Decant clear solution through a filter and wash by decantation with ammonia water (1 : 3). Dissolve the precipitate by pouring a little hydrochloric acid (sp. gr. 1·12) through the filter, allowing the acid solution to run into the beaker containing most of the precipitate. When all the precipitate on the filter and in the beaker is dissolved, wash the filter-paper with a little hot water. To the solution add 2 cc. magnesia mixture and then strong ammonia, drop by drop, with constant stirring until distinctly ammoniacal. Stir several minutes, then add strong ammonia equal to one-third of the liquid, let stand two hours, and filter off the precipitate of magnesium ammonium phosphate. Wash with dilute ammonia water, dry the precipitate, ignite separately from the filter, first at low temperature, and gradually raise to full blast. Weigh precipitate as $Mg_2P_2O_7$ and calculate as P_2O_5 in sample.

FLUXES AS APPLIED TO THE BRASS FOUNDRY.*

By ERWIN S. SPERRY.

In the early days of brass founding two things were guarded jealously: the mixtures and the fluxes. At that time it was not an uncommon occurrence to hear one say, when speaking of a new proprietor of a brass foundry, "He will get along all right. His father left him all his formulas for mixtures and fluxes." It seemed to be taken for granted that even capital itself was subsidiary to those heirlooms. Soon the chemist began to make serious inroads into the mixtures, and their secrecy faded away gradually but surely. The mystery of the fluxes was more difficult to eliminate, as, unlike the castings themselves, they did not go beyond the foundry. They could not be analysed without obtaining at least a small quantity, and this was difficult to do, as the brass founder carefully guarded them and the materials from which they were made. In the course of time, however, the secret fluxes went the way of the brass mixtures, so that by the process of evolution "secrets" finally became general technical knowledge. Few brass founders are now found who claim to have anything original or remarkable in the flux line.

When fluxes are mentioned, it is frequently asked, What is their advantage, and are they actually necessary? To answer this question, I will say that I believe the flux question is greatly overdone and likewise imperfectly understood. It was only a short time ago that I discovered a brass founder using lime in making an 88-10-2 mixture from new metals. He said "somebody" had told him that it was good for bronze. Although cheap substance that it is, he was wasting his lime, as it remained on the metal like so much dirt, and had no more effect than sand. In another instance I found that a brass ingot maker used a couple of handfuls of a mixture of common salt and borax on the top of a pot of yellow brass after it had been skimmed and immediately before pouring. The mixture was thrown on and then at once skimmed off without waiting for the borax even to stop swelling. He, too, would have been equally as well off without the flux. Another, but diametrically opposite case, was a brass founder who attempted to melt his emery grindings in a crucible without a flux and obtained about a pint of metal and half a bushel of dross. In this case a flux was needed.

It hardly will be advisable to go into a detailed enumeration of all the fluxes known to mankind and that can be used in brass melting, as it would be of little value. Many substances once used for this purpose have now become obsolete, and many others have proven to be valueless. It seems preferable, therefore, to give a description of those fluxes that the test of time has proved valuable and the manner in which they should be used.

Flux for Aluminium.—For years those who melted aluminium used no fluxes at all on it, not even charcoal, as it was soon found that this material did more harm than good. On account of the lightness of aluminium, charcoal does not readily free itself, and is apt to become entangled in the metal and produce small black spots in the casting. It is within the past few years that a flux has become used.

For aluminium the flux that is most extensively used, and which has proved to be so valuable, is *chloride of zinc*. It seems to react with the aluminium, forming chloride of aluminium and metallic zinc, which alloys with the aluminium. When this takes place the dross is changed to a fine granular condition, which is readily skimmed off. When aluminium is melted, the surface is covered with a rather thick mass, but the chloride of zinc will change it to a perfectly clear one closely resembling in appearance molten tin or lead. It is needless to say that such clean metal gives better castings.

The method of using chloride of zinc as a flux in melting aluminium is simple. Small pieces are thrown on the surface after the melting has been completed. Enough has been added when the surface is clear. A very small amount usually suffices, and for 50 lbs. of aluminium a piece of the size of a walnut is generally enough. The metal is stirred immediately after the addition, and then skimmed. Those who have not used chloride of zinc should try it, as it is an excellent material.

Flux for Nickel—The flux used by makers of nickel anodes has proved to be a good one. It was first used by A. M. Hill, of New Haven, Conn., one of the first in the United States to make nickel anodes and the inventor of the well known "Hill-Barrel" for grinding brass furnace ashes. Mr. Hill has retired from the anode business, but for many years he used this flux with the best results. It is not only good but cheap. It is composed of the following:—

Lime	3 parts
Fluor-spar	1 part

The manner of making it is to take the lime and slake it as though mortar were to be made. Then stir in 1 fluor-spar and allow it to become solid. It is then broken up into small pieces for use.

While fluor-spar alone is a good flux, it becomes very fluid when melted, and rapidly attacks a crucible. I have seen a new plumbago crucible ruined in one heat when fluor-spar was used alone. It seemed to soak in and dissolve out the clay from the crucible mixture and leave nothing but the graphite. The crucible collapsed like an egg shell when grasped with the tongs. The use of the lime with the fluor-spar is to increase the melting-point so that it will not so readily attack the crucible. The proportions previously mentioned have been found satisfactory for nickel. Less lime will render it more fusible.

This flux has been found particularly serviceable in melting old anodes, as it dissolves any earthy matter that may be on them. It is used for both new and old material, however, and may be called the standard flux for nickel. The proportions used are about a pint or a good handful for a new nickel, and twice this quantity for old material.

It must not be imagined because the fluor-spar is toned down with lime that the flux will not act on the crucible, for it certainly will. The crucibles last only five or six heats. In this connection it should be borne in mind that all fluxes act on the crucible to a greater or less extent, otherwise they would not be of value as a flux.

Flux for Copper.—There probably have been more fluxes proposed or used for copper than for any other metal or its alloys. The fact that copper cannot be melted alone and obtain sound castings from it has brought about this fact. Practically every known chemical has been tried. In the selection of a flux for copper it should be known whether pure copper castings are to be made, or whether it is to be alloyed to make brass or bronze.

To make sound copper castings with a flux alone, and without the use of "physic" like silicon-copper, magnesium, or similar materials (which strictly speaking are not fluxes) is a difficult matter. For this purpose I have found that yellow prussiate of potassium (potassium ferrocyanide) is excellent. With it sound copper castings can be made, but I do not advise it, as far better results may be obtained by the usual deoxidising agents, such as silicon-copper, magnesium, phosphorus, &c.

In melting copper for producing brass or bronze, the question is different from the preceding one. For this purpose there is nothing better than *common salt*. Its value lies in the fact that it possesses the property of reducing any oxide of copper which may form during the melting. It has been used for years in the brass industry, and the memory of the "oldest inhabitant" fails to indicate the date of its inception.

Common salt is so efficacious in reducing oxide of copper that, as far back as 1882, R. Monger in the Chemical News proposed it as a means for determining the quantity of oxide that copper contains. His method

* Paper read before the American Brass Founders' Association.—From the *Chemical Engineer*, xii., No. 6.

was to melt salt in a clay crucible and then drop in the weighed sample of copper. After allowing it to remain for a short time, the crucible was cooled and broken, when the button of pure copper was obtained. The difference in weight gave the amount of oxygen (or its equivalent of oxide of copper). Some very satisfactory results were cited.

In melting the copper for making brass or bronze, about a handful of salt is used and is preferably put in after it has begun to melt. If introduced with the copper, it melts before it, and is apt to volatilise and waste. The action on the crucible is also greater. Too much salt produces a liquid that is apt to penetrate the crucible, like fluor-spar, although not as violently or as rapidly. The amount of salt previously given is used for a pot of metal holding about 150 lbs. The quantity need not be exact, as a variation either way does no harm as long as a sufficient quantity is used to do the work.

The theory of the action of the common salt seems to be that, at the temperature of the molten copper, it breaks up or dissociates into metallic sodium and chlorine gas. The latter escapes and the sodium performs the work in deoxidising.

Flux for Brass.—The flux almost universally and exclusively employed in brass melting is *common salt*. As previously mentioned, its action is to reduce the oxide of copper formed in melting the copper previous to the addition of the spelter. The brass rolling mills in the Naugatuck Valley, Connecticut, and elsewhere as well, all use it, and one large company uses approximately half a ton a day. It is the universal and only flux used in making brass for rolling. For years it has been employed for this purpose, and in my own remembrance always has been. It seems to give all that is desired and has the distinct advantage of being cheap. Any kind of salt will answer, and a pure material is unnecessary.

The quantity used is about a handful to the crucible. One concern uses one handful, while another believes that double this quantity should be used. A good-sized handful, however, seems to be sufficient. It is added after the copper begins to melt, as this appears to be the best time to introduce it. When the right conditions have been produced, there will be a little slag on the top of the brass when it is skimmed.

It is worthy of note that, although every brass rolling mill uses salt in brass melting, few brass founders who make sand castings employ it. Many of them never have heard of it, and others seem to think it is a waste of time. I advocate its use under all conditions, and as it is theoretically correct, has been found by actual practice to improve the quality of the brass, and is so cheap that the cost of the brass is not appreciably increased, it seems to me that every brass founder should use it, whether he makes new metal or melts scrap, as the character of his castings will be improved.

Flux for Bronze and Composition.—What has been said about the use of *common salt* in melting yellow brass, applies equally well to composition or bronze, and it is used in identically the same manner and in the same quantities. It makes no difference whether phosphorus or other deoxidising agents are employed, the salt is used just the same.

Flux for German Silver.—German silver is such a refractory material in the rolling mill that much time and thought have been given the subject of a suitable flux for it. It is a singular fact that the bulk of the German silver manufactured in the United States is made by two concerns. One uses a flux in making it, while the other uses none. In justice to the concern which uses no flux at all, I will say that their German silver has a little better reputation and they have the more particular trade. I cite these examples simply to indicate that fluxes do not constitute the "secret" of making German silver by any means.

The use of the flux by the other concern dates back to 1869, when Frederic Wilcox, a brass caster, who was engaged in making German silver, had trouble with black minute spots in his metal. Tradition states that he gave the matter much thought, and finally believed it was caused by carbon in the metal. More "thought" indicated to him that the only method of removing it was to use a nitrate of some kind which would evolve oxygen and oxidise the carbon. Nitrate of soda, therefore, was used, and upon its use in the German silver he obtained a patent (U.S. Patent No. 96,524, Nov. 2, 1869). As this material was found to work better with black oxide of manganese, the two afterwards were used together and now constitute the flux of the aforesaid concern.

Personally, I doubt whether this flux has much value, and the fact that it is possible to make good German silver without it would seem to indicate it. I feel quite sure that there is no oxidation of carbon, as nitrate of soda, when allowed to melt on copper, will not oxidise it; but instead will actually render it sounder. It is also a singular fact, which I have already demonstrated in practice, that a mixture of nitrate of soda or the nitrate of potash (nitre), mixed with black oxide of manganese and used as a flux on copper, will actually introduce metallic manganese into the copper, showing that there is a reducing action. This explains, I believe, the reason for the action of the flux. A slight amount of manganese is introduced. This is also borne out by the fact that, within the last few years, metallic manganese has come into use as a deoxidising agent for German silver and similar nickel alloys. It use is preferable to introducing manganese through the agency of a flux, as the results are then positive and certain and predetermined amounts of manganese always can be added. Its use has been attended with excellent results, and it seems to be the natural deoxidising agent for nickel and nickel alloys.

In making German silver common salt is used in the same manner, and with the same results, as those obtained in brass and bronze.

Fluxes for Washings, Grindings, &c.—In the melting of washings from the reclaiming of brass foundry ashes, a flux must be used in the majority of instances, unless they have been washed very clean, and this is rarely done. Even with clean washings a flux is advisable. The same rule applies to grindings skimmings, and similar waste materials. Unless a flux is used when they are melted, a union of the particles of metal is prevented by the presence of so much foreign matter, and instead of fluid metal there usually is obtained a small quantity in the bottom of the crucible, and a large mass of pasty material fritted together. When a flux is used the foreign matter is dissolved, and clean metal is left.

For use in melting brass, bronze, or composition washings, grindings, skimmings, and similar material, I have found nothing better than *plaster of Paris*. It is a cheap and excellent flux for this purpose. How far back it was employed for this purpose I cannot say, but it was first called to my attention in 1890 by the late C. S. Moore.

With due respect to the late C. S. Moore, I believe he can really be called the father of the present scrap metal industry in the United States, as he was responsible for many innovations (like the "transmutation" of yellow washings into red), and I firmly believe he was the first to use plaster of Paris as a flux. He informed me to this effect, and I have no reason to doubt his word.

The value of plaster of Paris as a flux in melting washings, grindings, and similar material is that it possesses the property of dissolving what foreign matter may be present in the shape of sand, slag, or oxide, and it has practically no action on the crucible. In addition it is quite cheap. On account of the fact that it has no action on the crucible, any desired quantity can be used. It melts readily and forms a thin slag.

To melt washings or grindings with plaster of Paris, mix about 5 lbs. of it with the washings when they are placed in the crucible. Then melt in the usual manner. If the slag at the conclusion of the melt is not sufficiently fluid, more should be added. When the metal is com-

pletely melted pour the entire contents of the crucible into ingot moulds. *Do not attempt to skim it.* The slag will run into the moulds with the metal and rise to the top. Allow the mass to cool, and then dump the ingot moulds. The slag of plaster of Paris can be readily detached by a blow from a hammer, or it usually will fall off under normal conditions. If desired, it may be used again. It will be found a very satisfactory flux for this purpose.

Plaster of Paris is calcium sulphate, and when used as a flux the action seems to be one of simple solution: The molten plaster dissolves the foreign matter as sugar is dissolved by water.

When coal is present in washings, as it usually is, there is a slight reduction of the sulphate to sulphide, and there will be an odour of sulphur during the melting. This seems to do no harm, and I have never been able to find that it injures the metal. In fact, it appears to act in an opposite manner, and any iron that may be present is changed to sulphide and enters the slag. I have always advocated the use of plaster of Paris in melting scrap materials containing iron, and have invariably found it to be followed by good results.

Necessity of Charcoal.—I have made no previous mention of the use of charcoal for the reason that it is not properly a flux, although it takes the place of one. I can say without hesitation that charcoal should be used as a covering in melting all the metals previously enumerated except aluminium. Its value lies in the fact that in burning it supplies a reducing atmosphere, and thus prevents the oxidation of the molten metal. At the same time it covers the metals and prevents the products of combustion from coming in contact with it. It is free from sulphur, which renders it the ideal material for this purpose. It should be coarsely granulated, and not powdered, so as to allow its covering the metal completely without danger of immediate combustion. Fine coke or coal, although frequently used, is much inferior to charcoal, as it contains more or less sulphur, which injures fine grades of metal.

REDUCTION OF TIN DROSS IN AN ELECTRIC FURNACE.*

By R. S. WILE.

Electrical heat was resorted to for the smelting of tin dross because of the fact that the heat could be internally applied to the slag, which is on the bottom of a shaft-type of furnace, thus enabling the dross to be thrown on top of the slag instead of being mixed with it as is done in the old style of furnace. The dross, being on top, comes in contact with the slag only at the point of reduction. The liberated gases filter through the dross, while any tin oxide which is volatilised is condensed in the colder portion of the dross, which, as I have said, is on top of the slag. The globules of tin produced in smelting pass downward through the slag and lose most of the impurities, so very little refining of the resultant product is necessary.

In operation, the top carbon, which is movable, is brought into contact with the lower carbon, which is stationary, and an arc formed. The slag is fed in and melted, and the carbon is raised until the desired amount of slag is added. The dross, mixed with the right percentage of carbon, is added, and the tin tapped from the bottom from time to time. The loss of tin has been kept as low as 0·25 per cent, and the average below 1 per cent. The amount of tin recovered varies largely on account of the varying percentages in the drosses treated. The average is about 2500 lbs. (1100 kg.) per day.

The plant consists of two furnaces, connected in series, both being 20 ins. (50 cm.) in diameter and 80 ins. (200 cm.) high inside, two 50 kw. transformers, and necessary electrical apparatus. In operation they consume about 44 kw. During the run it is desired to keep the amperage as near constant as possible, the voltage varying. At the start the voltage of each furnace is about 80, but toward the end, as the slag becomes less refractory, due to the combination of the iron and zinc of the dross and the slag, the voltage of each furnace will drop as low as 45—50. This and an analysis of the slag denotes the end of the operation, and the slag must be drawn out and new put in. This is done alternately with each furnace. The furnaces run continuously until time to be re lined, which is about every three or four months.

* Paper presented at the Eighteenth General Meeting of the American Electrochemical Society, in Chicago, October 13—15, 1910.—From the *Chemical Engineer*, xii., No. 5.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 12th, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Absolute Expansion of Mercury.*" By Prof. H. L. Callendar and H. Moss.

"*Density of Niton (Radium Emanation) and the Disintegration Theory.*" By Dr. R. W. Gray and Sir W Ramsay, K.C.B., F.R.S.

"*Charges on Ions in Gases, and some Effects that Influence the Motion of Negative Ions.*" By Prof. John S. Townsend, F.R.S.

The experiments on charges on ions in gases which had previously been made with air only have been extended to oxygen, hydrogen, and carbonic acid. The value of the quantity Ne for the negative ions is in all cases very near the value $1{\cdot}22 \times 10^{10}$, which corresponds to a charge, e, equal to the charge on a monovalent atom. The ions were produced by secondary Röntgen rays, and it was found that when non-penetrating rays were used the value of Ne for the positive ions was practically the same as for negative ions, but is much larger when the penetrating rays are used, showing that in this case some of the positive ions have double charges.

The motion of the negative ions is considerably changed by carefully drying the gases, and the results of the experiments may be used in conjunction with the determinations of the velocities made by Mr. Lattey, to determine the apparent mass of the negative ion, which diminishes at low pressures as the electric force is increased. For a given force the pressures at which the effect of drying becomes appreciable is higher in hydrogen than in oxygen, and much less in carbonic acid than in the other gases.

"*Distribution of Electric Force in the Crookes Dark Space.*" By F. W. Aston, B.Sc., A.I.C.

The method used in the investigation is one due to J. J. Thomson, and consists in shooting a beam of homogeneous cathode rays transversely through the discharge, and observing the deflection of the beam at various points. The results so obtained are free from the very serious objections which may be urged against the "sounding point" methods used by previous observers.

The electric force in the negative glow is found to be negligibly small, while within the Crookes dark space it is satisfied within experimental error by the simple formula $\mu (D - x)$, where D is the length of the dark space, x the distance from the cathode, and μ a constant. This result indicates the presence of a uniform charge of positive electrification within that region. The distribution is the same for all gases, pressures, and currents used.

By integrating the forces so obtained the potential fall across the dark space is calculated, and is found in all cases to agree within experimental error with the actual potential

between the electrodes. The large and abrupt fall of potential at the surface of the cathode found by other investigators is probably a result of faulty methods, an explanation of which is suggested.

"*Measurement of End-standards of Length.*" By Dr. P. E. SHAW.

A continuation of work published in *Roy. Soc. Proc.* December 1, 1905). In recent years the authorities at the National Physical Laboratory have been required to measure and test end-standards with unprecedented accuracy. As a result, the faults of the standards and of the measuring machines have come to light. In this paper an account is given (1) of improvements in the planeness and parallelism of the standards; (2) of changes introduced in the writer's measuring machine to cope with the more accurate standards. It is easy to get consistent readings of length provided the standard is not moved; but if, as is required, the standard is moved, it is a difficult mechanical problem to provide a movement so nearly parallel that the readings before and after movement shall be consistent. Curves and tables are given showing the degree of accuracy at present obtained. A great advance in refinement is expected on the present lines of work.

NOTICES OF BOOKS.

An Introduction to the Chemistry of Colloids. By Dr. VICTOR PÖSCHL. Translated from the Second, Enlarged, German Edition by HERBERT H. HODGSON, M.A. (Camb.), B.Sc. (Lond.), Ph.D. (Heidelberg). London: Charles Griffin and Co., Ltd. 1910.

DR. PÖSCHL'S excellent little book on colloidal chemistry has reached its second edition in German, and English students, teachers, and works' managers will welcome this translation of it. Although from limitations of space it can give only a sketch of the essentials of the subject, as a short general summary it is eminently successful, and the author has made a good selection of the facts and theories to be included for discussion and has adopted the most effective and graphic way of treating them. After studying this book the reader should be quite well able to understand the advances of the subject as described in original papers and in larger works. The chapter on the importance of colloidal chemistry in other sciences touches upon the applications of colloids and their peculiar properties in technology, and may be specially mentioned as an excellent little summary of the subject.

Technical Mycology. By Dr. FRANZ LAFAR. Translated by CHARLES T. C. SALTER. Vol. II. *Eumycetic Fermentation.* London: Charles Griffin and Co., Ltd. 1910.

THE delay in the appearance of the second volume of this treatise has been caused partly by the dilatoriness of the German publishers in supplying the final sheets, and partly by the magnitude and tediousness of the task of the translator, who has, however, finally succeeded in accomplishing his aim and has made a valuable text-book of mycology accessible to English readers. The second volume deals with eumycetic fermentation, and gives a complete account of the culture of yeast, the life history and morphology of the saccharomycetes, ascomycetes, and the Fungi Imperfecti. The general editor is responsible for only a small section of the book, and has had the advantage of the collaboration of authors who are well known for their research work in mycology. The volume contains the complete bibliography and index to the whole work.

Sketch of a Course of Chemical Philosophy. By STANISLAO CANNIZZARO (1858). Edinburgh: The Alembic Club. 1910.

THIS volume of the Alembic Club Reprints is a translation, to publish which permission was obtained from the author just before his death in May, 1910, of a letter which he wrote to Prof. S. de Luca, and which appeared originally in "Il Nuovo Cimento." In this letter he gave an admirable summary of the course of lectures on chemical philosophy which he delivered at the Royal University of Genoa; he explained very carefully and succinctly the steps by which he led his pupils to appreciate the true meaning and value of Avogadro's hypothesis and its application for the determination of atomic weights, and so excellently planned and clearly expressed were the lectures that they may with profit be studied by present day students. The reprint is by no means the least interesting and valuable of the series to which it belongs, and it deserves a wide circulation among students and also among teachers who wish to get an insight into the most satisfactory way of leading their classes to appreciate the historical development of chemical theory.

A Manual of Practical Inorganic Chemistry. By A. M. KELLAS, B.Sc. (Lond.), Ph.D. (Heidelberg). London: Henry Frowde; Hodder and Stoughton. 1910.

EVERY page of this book shows that its author has a thoroughly practical knowledge of teaching chemistry. He is under no illusions as to the amount of common sense to be expected from the average student, and he makes every allowance for carelessness and want of caution in dealing with dangerous substances. A great number of preparations is described in detail, and a complete summary is given of the inorganic compounds in the British Pharmacopœia, with tabular statements of the impurities which may be present. Part I. concludes with a course of qualitative analysis, which includes all the common acids and bases. The reactions of each metal are summarised, and the appearance, special properties, solubility, and methods of preparation of every compound met with in elementary analysis are tabulated. The second part of the book deals with quantitative analysis; typical gravimetric and volumetric processes being described, with the rudiments of gas analysis. The book completely covers Preliminary and Intermediate University courses and the first three stages of the syllabus of the Board of Education.

Iron and Steel Analysis. Volume I. By A. CAMPION, F.I.C., F.C.S. Glasgow: Fraser, Asher, and Co., Ltd. 1910.

THIS small book can be recommended for the use of evening students of practical chemistry, or of others who wish to obtain an elementary knowledge of the methods of iron and steel analysis in the shortest possible time. It is to be the first of a series of books on iron and steel analysis written by the author, and takes into consideration none but the ordinary constituents, *e.g.*, silicon, carbon, sulphur, phosphorus, &c. As a rule one method only is given for each constituent, and that is described in sufficient detail for the average student to carry out the determinations either without any or with very little supervision from a teacher. The methods selected are those usually employed, and may be regarded as the most rapid and accurate known, and in every case the method of working out the results is carefully explained.

Diet and the Maximum Duration of Life. By CHARLES REINHARDT, M.D. The London Publicity Co., Ltd.

THIS book represents an attempt to set forth the general principles by which almost anyone can obtain and preserve digestive health. It is written in a distinctly partisan spirit, but at the same time the author has some valuable suggestions to make regarding the adoption of dietaries both for healthful people and in disease. He gives some information as to the composition and value of many different foods, and shortly discusses the comparative advantages of vegetarianism and a mixed diet. He lays great stress upon the value of some branches of sour milk, and has a good deal to say on lactic bacterium therapy.

CORRESPONDENCE.

GRIFFIN'S CHEMICAL HANDICRAFT.

To the Editor of the Chemical News.

Sir,—In your issue of January 6th, commenting on our new catalogue "Scientific Handicraft" you say:—"Messrs. Griffins are to be congratulated on having included the description of all their manufactures in one volume."

As this may be somewhat misleading to some of your readers, we should like to point out that the catalogue to which you refer deals with physical apparatus only; we are at present at work on a new edition of our "Chemical Handicraft" dealing with chemical, metallurgical, and bacteriological apparatus, which we hope to publish next month, and which will form a companion volume to "Scientific Handicraft."—We are, &c.,

John J. Griffin and Sons, Ltd.

Kingsway, London, W.C., January 13, 1911.

A RAPID METHOD FOR THE IDENTIFICATION OF GAS OILS.

To the Editor of the Chemical News.

Sir,—In the Chemical News for January 6th, 1911 (vol. ciii., p. 3) there, appeared a paper by Park and Worthing on the "Identification of Gas Oils," which is reprinted from the *Chemical Engineer*.

The idea of using the bromine absorption test for this purpose was tried by us as far back as 1902, and was found to be unsatisfactory, as a considerable amount of secondary reaction undoubtedly takes place, and the amount of hydrobromic acid formed is not really a measure of substitution.

Further, we have shown that the dehydrogenated naphthenes do not react quantitatively with either bromine or iodine. Thus, tetrahydronaphthalene after twelve hours only absorbs the equivalent of rather over one atom of a halogen instead of six.

Further, the bromine absorption of any gas oil is not a constant unless the same limits of boiling-point are always adhered to. This, of course, is never the case in practice, the proportion taken for gas oils being dependent on the demands of the market for other classes of oil.

The effect of variations in range of distillation can be readily seen in the accompanying table, which is drawn up from experiments made in 1902, the results of which have not previously been published.

For the recognition of gas oils we have found (*Soc. Chem. Ind.*, May, 1902; *Analyst*, Sept., 1906, and July, 1907) that a distillation test in which the fractions are separated at intervals of 20° C. in such a way as to have an even number for the second digit, combined with the determination of the specific gravity, refractive index, and specific refraction of each fraction, affords not only reliable information as to the origin of the oil, but also as to its suitability for gas making purposes.

To see the reason of this it is only necessary to remember that the following facts hold good when comparing fractions of similar boiling-points obtained from different oils.

Open-chain compounds (paraffins) have the best value for gas making purposes, the lowest specific gravity, the lowest refractive index, and a moderately high specific refraction.

The presence of double bonds in the chain slightly decreases the gas making value, raises slightly the specific gravity and refractive index, but considerably lowers the specific refraction.

As regards naphthenes, their utility for gas making purposes depends entirely on their degree of hydrogenation.

Bromine Substitution and Addition (McIlhiney Process).

Boiling-point (C.).	Substitution.	Addition.
	Russian Refined.	
149—155	4·1	8·7
155—171	5·1	9·0
171—177	7·1	8·5
177—182	10·0	3·1
182—193	9·9	5·7
193—198	10·9	9·7
198—210	11·3	9·8
210—221	13·7	6·5
221—237	13·5	6·3
237—254	13·2	5·5
254—276	15·8	13·0
276—293	23·2	8·0
	Russian.	
225—245	15·0	3·8
245—265	14·8	1·6
265—275	12·1	2·6
275—295	8·8	4·1
295—295	9·7	4·8
295—305	8·0	4·3
305—330	11·7	1·0
330—350	11·1	1·6
350—360	10·8	3·3
360—370	11·3	1·3
370—400	13·0	1·2
400—430	14·2	4·7
	Borneo.	
170—175	22·8	4·3
175—180	22·3	4·5
180—187	22·1	4·4
187—200	22·9	1·4
200—225	20·4	8·0
225—235	21·1	8·2
235—245	24·5	5·1
245—250	25·9	5·5
250—265	26·1	3·8
265—265	26·2	4·0
265—270	25·8	6·2
270—275	24·1	6 0
275—280	25·7	5·2
280—285	23·9	9·7
285—290	26·6	5·3
290—300	26·3	6·2
300—320	25·7	3·7
	American (Pennsylvanian).	
150—200	30·1	22·5
200—250	32·0	12·6
250—280	32·6	2·9
280—300	33·7	—
300—310	32·5	—
310—315	33·2	—
315—320	33·2	—
320—325	33·6	—
325—330	33·0	—
330—340	33·2	—
340—350	37·3	—
350—360	18·5	13·0
360—370	18·4	11·6
370—375	13·8	23·7
375—380	18·3	15·6
380—400	17·8	17·3
400—420	17·7	21·8
	Texas.	
200—222	15·6	—
222—249	17·2	—
249—266	18·3	—
266—276	31·6	—
276—288	24·7	—
288 299	33·4	—
299—310	30·1	—
310—326	25·0	—
326—350	23·9	3·5
350—382	23·3	5·6

Saturated naphthenes, *e.g.*, of the type of deca-hydronaphthalene, are fair gas makers, but those of the type of tetra-hydronaphthalene are almost useless whatever temperature is used.

Naphthenes must, of course, differ within themselves; thus, there is no doubt that two isomeric substances might differ very greatly in their gas making value if one contained a number of small side-chains and the other one long side-chain. The more the paraffin of the side-chain predominates over the simple or conjugated benzene nuclei the better the oil for gas making purposes.

We are inclined to believe that the higher boiling ractions of most gas oils are largely made up of such naphthenes. The specific gravity and refractive index of such compounds would naturally conform to the rule that the longer the side-chain the lower the specific gravity and refractive index, and, conversely, the less hydrogenated, or the greater the predominance of the benzene nuclei, the higher the refractive index and specific gravity, always considered, of course, in relation to boiling-point.

It is thus possible to identify and value an oil with a very great degree of certainty if these points are kept well in view.

An examination of our papers already quoted will make the foregoing statements quite clear.—We are, &c.,

RAYMOND ROSS,
JNO. P. LEATHER.

Public Analyst's Office, Burnley,
January 11, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 23, December 5, 1910.

Decomposition of Hydrogen Peroxide by Light.—M. Tian.—The decomposition of hydrogen peroxide by heat is a bimolecular reaction. From the determination of the rate of decomposition when it is brought about by light it is found to be a monomolecular reaction. Thus it cannot be represented by the equation $2H_2O_2 = 2H_2O + O_2$, but to express all the facts the two equations $H_2O_2 = H_2O + O$, $2O + O_2$ are necessary. The action of light is thus quite different from that of heat, and seems analogous to that of a catalyser.

Brominated and Hydrobrominated Compounds of Silicon.—A. Besson and L. Fournier.—When a rapid current of dry hydrobromic acid acts on amorphous silicon heated to a red heat, from the raw product of the reaction the following compounds can be isolated by distillation and subsequent sublimation under reduced pressure:—1. $SiBr_4$. 2. A white crystalline solid fusing at 95°, distilling without decomposition under ordinary pressure at 265°, and having the composition represented by the formula Si_2Br_6. 3. A white crystalline substance of formula Si_3Br_8, fusing at 133°. 4. Si_4Br_{10}, which can be sublimed *in vacuo*, and appears to fuse at 185°; at this temperature it undergoes partial decomposition, leaving a white residue.

Reactions in the Electric Arc.—E. A. Salmon.—The author describes an apparatus for inducing two substances to react in the electric arc; it consists essentially of two electrodes pierced axially by channels; the gas is led down one channel and the products of the reaction escape by the other. Using this apparatus the author has made carbon unite directly with nitrogen, forming cyanogen, and water can be decomposed by copper.

Hydrogenation of Isomeric Thujenes and of Sabinene.—L. Tchougaeff and W. Fomin.—By the direct hydrogenation of α- and β-thujenes and of sabinene, hydrocarbons of formula $C_{10}H_{18}$ are obtained. They possess very similar physical properties, and apparently are saturated bicyclic compounds. Their composition is that of thujane, and the trimethylenic nucleus is evidently not altered by hydrogenation in presence of platinum black in the conditions specified by Wilstatter and Mayer.

New Reaction of Morphine.—Georges Denigès.—To 10 cc. of a solution of morphine chlorhydrate 1 cc. of hydrogen peroxide is added, also 1 cc. of ammonia, and then a drop of copper sulphate solution containing 4 per cent of the crystalline salt. If the whole is well shaken both before and after adding the copper salt a pink or red colouration appears. This reaction seems to be due to the phenolic hydroxyl of the alkaloid.

No. 24, December 12, 1910.

Action of Nitric Acid on Aloïns.—E. Léger.—When nitric acid acts on the aloïns the products are chrysammic acid, picric acid, and oxalic acid; the first of these, however, is not formed directly, but results from the transformation of an intermediate product, viz., tetranitro aloemodine, the formula of which is $C_{14}HO_2(NO_2)_4(OH)_2(CH_2OH)$. Apparently tetranitrorheine, $C_{14}HO_2(NO_2)_4(OH)_2(COOH)$, is first formed, and is then changed into chrysammic acid.

Hexahydroacetophenone and Hexahydrobenzoylacetone.—Marcel Godchot.—Hexahydroacetophenone when oxidised with permanganate gives adipic acid. It reacts very readily with hydroxylamine chlorhydrate in presence of potassium carbonate, giving the oxime, $C_6H_{11}—C(NOH)—CH_3$. The isomerisation of this oxime yields hexahydroacetanilide, $C_6H_{11}.NH.CO.CH_3$. When hexahydroacetophenone reacts with acetic ether in presence of sodium ethylate, hexahydrobenzoylacetone, $C_6H_{11}.CO.CH_2.CO.CH_3$, is formed; it is a colourless liquid with a very penetrating odour.

No. 25, December 19, 1910.

This number contains no chemical matter.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Royal Society of Arts, 8. (Cantor Lecture). "Etching," by F. Wedmore.

TUESDAY, 24th.—Royal Institution, 3. "Heredity," by Prof. F. W. Mott, F.R.S., &c.

WEDNESDAY, 25th.—Royal Society of Arts, 8. "Motor Transport in Great Britain and the Colonies," by Horace M. Wyatt.

THURSDAY, 26th.—Royal Society. "Memoir on the Theory of the Partitions of Numbers—Part V., Partitions in Two-dimensionals Space." by Major P. A. MacMahon. "Origin of Magnetic Storms," by Dr. A. Schuster. "Fourier Constants of a Function," by Dr. W. H. Young. "Energy and Distribution of Scattered Röntgen Radiation," by J. A. Crowther. "New Facts connected with the Motion of Oscillating Water," by Mrs. H. Ayrton.

— Royal Institution, 3. "Recent Progress in Astronomy," by F. W. Dyson, Astronomer Royal.

FRIDAY, 27th.—Royal Institution, 9. "Radio-activity as a Kinetic Theory of a Fourth State of Matter," by Prof. W. H. Bragg, M.A., F.R.S.

— Physical, 5. Demonstration of Phase Difference between the Primary and Secondary Currents of a Transformer by means of a Simple Apparatus, by F. T. Trouton. "Experimental Measurement of the High-frequency Resistance of Wires," by J. A. Fleming. "Measurement of Energy Losses in Condensers traversed by High-frequency Oscillations" and "Some Resonance Curves taken with Impact and Spark Discharges," by J. A. Fleming and G. B. Dyke.

SATURDAY, 28th.—Royal Institution, 3. "Problems in the Career of the Great Napoleon," by Arthur Hassall, M.A.

THE CHEMICAL NEWS.

Vol. CIII., No. 2670.

THE USE OF CALCIUM CARBIDE FOR DETERMINING MOISTURE.*

By IRVINE MASSON, M.Sc.(Melb.).

In the determination of moisture in pure and in raw materials the methods which have been in use have generally proved accurate and reliable. They depend, for the most part, on removal of the water by heating the material, and measurement of the resulting loss of weight; sometimes the water driven off is collected and weighed. Often, however, the material dealt with is such that, when it is heated, it gives off vapours other than water; or it may be that some of the water evolved is the result of chemical decomposition. Again, certain substances gain weight by oxidation when heated in air. In all such cases it is obvious that weighing alone gives results which may lead to considerable error; other methods must therefore be sought which are free from objection.

The introduction of calcium carbide as a commercial article has afforded a means of moisture determination which overcomes the difficulties mentioned. Since, however, the method has not attracted such general attention as it deserves, an account of it may be of interest to chemists, technical and otherwise.

The great advantages of calcium carbide as a reagent in water determination may be summed up by saying that, of all substances dealt with in ordinary circumstances, water is the only one which has any chemical action on carbide; and this action is rapid, and generates a gas, whose quantity is readily ascertained and gives a direct measure of the action. The gas in question, acetylene, is produced according to Moissan's well known equation, $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$.

It is apparent, then, that a good method of water determination should be obtained by allowing a weighed amount of the material under consideration to give up its water to excess of carbide, and measuring the acetylene evolved.

Up to the present time applications of the foregoing principles have not been numerous. The first was described by H. A. Danne in 1900, before the Society of Chemical Industry of Victoria. Danne applied the method to various hygroscopic organic powders, for which the ordinary method of heating and weighing is unsuitable. The powder was weighed into a test-tube, and covered with a layer of sand, on top of which was a layer of carbide. On heating the tube, the moisture of the powder distilled through the sand, and acted on the carbide, generating acetylene, which was collected. The apparatus having been standardised with known amounts of water, the moisture in the material could be found from the volume of acetylene. A process which was substantially the same as that of Danne was described by P. V. Dupré (*Analyst*, 1906, xxxi., 213), for moisture determination in cordite and similar materials.

It is to be noted that in this process the water is brought into contact with carbide after removal from the original material by distillation. It has been found, however, that such a process is unnecessary; and in later work a large excess of the carbide is simply mixed intimately, in the form of powder, with the material under examination. By the natural processes of diffusion all the moisture present rapidly reaches and reacts on the carbide. This has been established by direct tests.

A method based on this fact is now in use in Australia for the determination of moisture in sheep's wool, having been devised at the instance of a joint conference of pastoralists and workers held in 1908-1909. A detailed account is given by Orme Masson (*Proc. Soc. Chem. Ind. Victoria*, 1909). In carrying out a determination a fixed weight of wool clippings is introduced into a metal globe, which has a screw top provided with a tray below, and with a gas-exit tube. On the tray is placed a charge of finely powdered carbide in considerable excess of the theoretical amount; when the globe is shaken this falls on to the wool, and is brought into intimate contact with it, causing immediate evolution of acetylene. The quantity of gas was formerly obtained by measuring its volume when collected at atmospheric pressure; it is now found more convenient to measure the increase of pressure at constant volume, by reading a mercury manometer attached to the metal globe. All instruments are made of standard capacity, and the manometer is graduated in percentages of moisture.

Only one other application of the carbide method to industrial materials seems to have been described, namely, that to petroleum containing water (Roberts and Fraser, *Journ. Soc. Chem. Ind.*, 1910, xxix., 197). In this process excess of carbide is allowed to fall into a fixed quantity of the petroleum, which may be rendered fluid by addition of dry paraffin oil. The volume of acetylene is measured by the quantity of brine which it displaces from a bottle, the necessary temperature correction being made. The results are stated to be reliable and accurate.

The applications of the method so far discussed concern the determination of water present as moisture; that is, mechanically mixed with the material. In some cases, however, water is present in another form, chemically united with the material as water of crystallisation, and the question arises, is the carbide method applicable to the determination of combined water? To investigate the action of calcium carbide on water of crystallisation, the writer carried out experiments with numerous hydrated salts (*Trans. Chem. Soc.*, 1910, xcvii., 351). A known weight of hydrate was mixed with excess of carbide powder, both being contained in a bent test-tube, the tilting of which brought about mixing; the gas generated passed into a nitrometer, where it was measured over mercury. Briefly, the results of the examination show that, as regards behaviour towards carbide, hydrated salts are roughly divisible into four classes. In the first are those, such as sodium carbonate and sodium sulphate decahydrates, which react at once and completely, being rendered anhydrous. Salts of the second class, such as barium chloride dihydrate, react rapidly and completely only on heating. The third class, which includes salts such as copper sulphate pentahydrate and the alums, react, either in the cold or on heating, in such a way as to lose only part of their water, leaving a hydrated residue which belongs to the fourth class, characterised by being quite stable towards carbide even at 170° C. In general, the stability is such as might be anticipated from the behaviour of the salts when they are heated alone; there are, however, interesting exceptions. It is noteworthy that ammonium salts do not lose ammonia, nor do crystalline acids react as such, when these are heated with carbide and the calcium hydroxide present as a result of the acetylene production; this is to be attributed to the complete absence of free water.

From the analyst's point of view, the carbide method as applied to hydrated salts is quite satisfactory for the first, second, and part of the third classes mentioned above. In those cases where the method cannot be applied, it has been found that the usual process of heating and weighing s also inadequate, and indirect methods must be used to determine the degree of hydration.

In conclusion, some instances in which the carbide method would prove of value may be indicated. These are mainly cases of technical materials whose water content is not easily obtainable by the ordinary means. For cotton,

* Read before the Australasian Association for the Advancement of Science, January, 1911.

paper, fabrics, wood-pulp, tobacco, flour, the "wet wool" apparatus would be specially useful; while the other instruments, suitably modified, would be applied with advantage in the cases of soils, minerals (*e.g.*, guano), and coal. Fatty substances, such as butter, cocoa, and the like, might be dissolved in benzene or some other suitable anhydrous liquid in order to facilitate the action of the carbide.

Whatever the particular apparatus, standardisation of the carbide with known quantities of pure water is necessary. It should be remarked, however, that in spite of wide differences of treatment, the yield of acetylene from a fixed weight of water acting on excess of commercial carbide has been found by different observers to be practically constant, namely, 10·5 cc. of gas at 0° C. and 760 mm. for every 18·0 mgrms. of water. The theoretical yield is 11·2 cc.

Enough has been said to show that calcium carbide affords a ready and reliable means for determining water, and is especially of value for that purpose with organic materials.

THE PURIFICATION OF WATER BY OZONE.
(Ozonair System).

The simplest and most certain method of purifying drinking water is sterilisation by ozone. It accomplishes its purpose without in any way altering the natural constitution of the water and at the same time leaves no trace of its presence. Water which previously was alive with dangerous organisms will after proper subjection to ozone treatment be in perfect condition for consumption. Moreover, its appearance and odour have been improved, and it will have a sparkling brightness which before the treatment was absent.

In the methods hitherto adopted for effecting the sterilisation of water by means of ozone, mutual contact between the water and the gas has been made dependent upon either exposing the liquid in a thin film to the action of a current of the gas, or upon forcing the gas through the body of the liquid.

By neither of these methods is it economically practicable to ensure a perfect result on a commercial scale, and the object of the Ozonair system is to provide an improved method and means whereby, so far as possible, thorough mutual contact may be simply and economically ensured between the liquid and the gaseous agent.

In the Ozonair system the water is first atomised in presence of a stream of ozonised air within the upper portion of the apparatus, the minutely divided particles of liquid being allowed to fall upon the upper part of a pile of glass spheres, through the interstices of which the stream of ozone is caused to ascend whilst the liquid, already partially ozonised and sterilised, descends over the surfaces of the spheres in a very thin film.

On reaching the bottom of the pile the water is allowed to fall into a tank through which the ozonised air is forced upwards in fine jets, the water being retained in the tank and subjected therein to this third ozonising process for any predetermined length of time according to requirements.

It will be obvious from the above description that the Ozonair system ensures sterilisation, and that by no means can any portion of the water, however small, escape contact with the sterilising agent at some portion of its descent in the tower.

The Ozonair system ensures the best treatment at the proper time, for the reason that, as the water descends through the tower, the concentration of the ozone gets more intense, until when, having fallen into the tank, it is subjected to a stream of ozonised air coming direct from the generator.

The living bacilli falling into the tank are the most resistant and therefore need the strongest treatment.

SEPARATION OF OXYGEN BY COLD.*

By James Swinburne, F.R.S.

This industry has arisen, almost by accident, out of that of the liquefaction of gases. It had long been the ambition of scientific men to liquefy first one gas and then another; the liquefaction of such gases as oxygen, hydrogen, and nitrogen being a sort of North Pole to be reached. It is doubtful whether reaching the North Pole is of any value to anybody but newspaper men, whereas the production of very low temperatures was bound to increase our knowledge very materially. Like most researches that appear at first to have purely increase of knowledge value, low temperature work has proved to be, in addition, of direct commercial importance.

Though the separation of gases by cold has arisen out of the liquefaction of air, the two problems are not quite the same. Leaving out of account the details of the machine employed for the moment, we may consider the apparatus as a closed vessel, insulated to prevent heat getting in through the walls, and having three pipes. In at one pipe we may assume that air at the temperature of the room, but at a higher pressure, enters the machine; at a second and third, oxygen and nitrogen come out at the pressure and temperature of the room. Air under high pressure has less internal energy than the same mass of air at the same temperature and lower pressure, so that if air is continually going into the apparatus at the temperature of the room and at high pressure, and its constituents are coming out at the same rate at the temperature and pressure of the room, more energy is coming out of the apparatus than is going in. This is impossible as a permanent regime. It cannot be put right by less air coming out than goes in, because that would mean an accumulation of air. A balance can be obtained by taking out most of the air at the pressure and temperature of the room, with a higher internal energy per kilo, while a little of the air comes out at a low temperature, with less internal energy per kilo. This portion may be quite small, and may be liquid.

But the air is supplied under pressure, and comes out at the pressure of the atmosphere, so it must be expanded inside the apparatus, and as there is no way of getting the energy of expansion out of the apparatus as described, it must be converted into heat, provided it is expanded irreversibly. This means loss of power, which is a small point, and production of heat just where it is not wanted, which is a serious matter. If, therefore, in addition to the three pipes, there is communication by a shaft, and the apparatus may be arranged so that the expansion of the air works some sort of engine which turns the shaft so that work is given out, the yield of the liquid air must be larger. The ideal liquid air machine would therefore take in compressed air and give out air at the same temperature, but at the pressure of the atmosphere; and a stream of liquid air, and as much power as possible, would be given out mechanically through a shaft or other mechanical transmitter. It will be explained presently that the Linde separation process is nearly reversible, capable of being but little improved by giving out energy.

It is generally assumed that the problem of the separation of gases is substantially the same. This is not the case, however, and the overlooking of the difference has led inventors and designers of such apparatus into a series of absurd mistakes.

Take the ideal apparatus for separating gases; we have a pipe leading in gas under pressure at the temperature of the room, and two pipes coming out; one carrying oxygen more or less pure and the other nitrogen more or less pure, at the temperature and pressure of the room. Now the internal energy of the gases coming out is greater than that of the compressed gas going in, and if the energy were alone to be considered, once the apparatus was started and got into running order as regards temperatures, air

* A Paper read before the Faraday Society, December 13, 1910.

might go in at the pressure and temperature of the atmosphere, and come out as oxygen and nitrogen at the temperature and pressure of the atmosphere, the process being continuous and costing nothing appreciable. But as the apparatus cannot be made quite heat-tight in practice, the air might have to go in under slight compression, so as to have slightly less internal energy than the gases coming out; the difference being just enough to compensate for the leakage of heat through the casing of the apparatus. This is an ideal apparatus which several inventors have designed; but it is not possible to make such an arrangement work.

The energy is not the only quantity to be considered. Let us return to the simple case of an apparatus which is perfectly heat insulated, fed with air at the pressure and temperature of the room, giving out oxygen and nitrogen separately at the same temperature and pressure. The entropy of the separated gases is less than the entropy of the air going in, so if the process is continuous there must be a continual disappearance of entropy inside the apparatus, which is not thinkable. Air at a higher pressure, but at the temperature of the room, has less entropy, so it may be supposed we can get things right by compressing air until it has the same entropy as a compressed mixture as the issuing gases have as they come out. We would then have an entropy balance. This will not suffice in the ordinary course, however, because the compressed air must be expanded, and if that is done irreversibly inside the apparatus, more entropy is produced there, and to make a proper entropy balance, either the expansion must be done reversibly, or air must be so compressed that its entropy is reduced below the sum of that developed by any expansion and that of the separate gases. Imagine this done; have we a thinkable machine? No, because now our energy balance is wrong; we have air going in with less internal energy than the gases coming out. It will be found on further consideration that the energy balance is got right by using imperfect heat insulation, heat leaking in to make up the extra energy of the issuing gases over that of the entering air; the entropy of the compressed air plus the entropy due to the heat leaking in, plus any entropy due to irreversible expansion or conduction of heat in the interchanger, being equal to the entropy of the gases coming out. If desirable the case may insulate perfectly, and some of the air or gases may be delivered continuously in the liquid state. The point to notice is that as the oxygen and nitrogen coming out have less entropy than if they were mixed at the same temperature and pressure, the apparatus has to be fed with compressed air, and energy is therefore needed to separate the gases. This point has been so often overlooked that it is necessary to dwell upon it. As far as I know I was the first to publish it.

It has sometimes been supposed that because the gases are separated at a very low temperature the data determining the energy necessary to separate them do not depend on the difference of entropy of the separate gases and the mixture at the temperature of the room, but at the temperature of separation. This is erroneous and may give rise to further mistakes. That it is erroneous is clear from the illustration. Suppose the difference of entropy of cold gases separate and cold gases mixed is less than the corresponding difference at the temperature of the air; even if the entropy of the entering air is reduced enough to compensate for this only, and not for the entropy of the issuing gases, the entropy balance of the machine as a whole is wrong. Heat leaking in is difficult to value, as there is an irreversible change as the heat is conducted to the cold gases, which means increase of entropy; and there is increase of entropy due to irreversible expansion. For simplicity take a heat-tight case, and the energy balance kept right by drawing out a small stream of liquid air. Then, if there is no irreversible process inside the apparatus, there is no growth of entropy in it; and the entropy of the gases coming out, plus the entropy of the liquid coming out, must be equal to the entropy of the air going in. In other words, the entropy balance depends on the entropy of the issuing and entering streams, and not on the entropy of the gases at some inside point where they are at very low temperatures, though the separation actually takes place there.

To make the matter clearer it may be better to put the entropy question more fully. The change of entropy of a gas may be split up into entropy of change of volume, which varies as the logarithm of the volume or of the free path of the particles, and entropy of change of temperature, which varies as the logarithm of the speed of the particles. We may call these two, the volume and the speed entropies, ϕ_v and ϕ_s. When two gases mix, the volume of each increases in a way—that is to say, it pervades a larger space, and the molecular free path of each particle is increased if you take into account the collisions with other particles of the same gas only. The mixture of two mutually inert gases thus involves increase of entropy, which I will call entropy of mixture, ϕ_m. As this depends solely on the logarithms of the free paths, it depends, in the case of two gases at the same temperature and pressure, only on the relative volumes of the gases before they are mixed.

There is still another point to be considered. If a perfect gas is, say, expanded at constant temperature, its internal energy remains the same; but such gases as oxygen and nitrogen have a slightly larger internal energy at the larger volume, as discovered by Thomson and Joule, and this involves an increase of entropy in excess of that due to the increase of mean path; this may be called the Kelvin entropy or the Joule entropy; preferably the Kelvin entropy, as the term joule, being used to denote the unit of heat, might give rise to confusion. We may call this ϕ_k, if a symbol is ever wanted.

We may imagine a closed apparatus with entry pipe for air and exits for nitrogen and oxygen. We have then air going in at one pipe and oxygen and nitrogen coming out at two others, and heat leaking in from the outside. The conditions for permanent regime are that the internal energy of the O and N coming out must be equal to the sum of the internal energy of the air entering and the heat leaking in. If this were all, of course we would arrange no heat leakage, and let the air come in and the oxygen and nitrogen come out at the pressure and temperature of the air. But we must get the entropy balance right too—that is to say, that the entropy of the oxygen and nitrogen coming out must be at least equal to the entropy of the air going in, and if heat is leaking in, or if there is any other irreversible process, such as free expansion going on inside, or irreversible conduction in the interchanger, the entropy of the gases coming out must be greater.

So many people are unfamiliar with this way of discussing such questions, that it may be better to deal with the matter also along other lines.

As the separation of the oxygen and nitrogen is carried out in a rectifier, we may discuss the action of the rectifier, taking an alcohol rectifier first as being more familiar, and not involving out-of-the-way temperatures; though, as a matter of fact, it is in a way much more troublesome to discuss.

Fig. 1 shows an ideal, or paper, diagram of an alcohol still reduced to a simple form. A mixture of 50 per cent alcohol and water at 0° C. comes in at E and flows through a heat interchanger G until it reaches 80°, the boiling-point of alcohol. It then passes up the pipe H to the top of the rectifier I. The pipe zigzags, or winds, down to a point where the temperature is 82°, the boiling-point of the mixture. The liquid is then discharged into the rectifier, which may be full of trays, and trickles down to the bottom and out by the pipe F, and thus to the interchanger G. The alcohol vapour comes off by the pipe K, and is nearly all condensed at L and passed to the interchanger. The water and alcohol come out at 0° C. at D and C.

The rectifier must have heat supplied at B to boil off enough steam to rise against the trickling fluid, and assuming all the parts of the apparatus heat-tight except where arrows are put, we have coming out of the system heat at A, where the alcohol vapour is condensed, and at

F, where the water coming out at 100° is cooled to 80° before entering the interchanger. As alcohol and water heat on mixing, the output from D and C have higher internal energy than the ingo at E, but except for that, all the heat that goes into the interchanger in the pure water and pure alcohol goes into the mixture and goes back into I by the pipe H.

Suppose the still deals with 1 kilogrm. of mixture per minute, 500 grms. of water come down the pipe L, so the heat given out in cooling the water to 80° is obtainable. The heat of mixture of water and alcohol gives the extra internal energy of the output. If the heat capacity of the mixture were the same as that of the alcohol and water separately, the water and liquid alcohol entering the interchanger would just heat the mixture to 80° as they cooled to 0°, but, as might be expected from their mixture evolving heat, the heat capacity, in which is really involved the disgregation energy, is higher. so either the water must be admitted above 80°, or the alcohol must not be all condensed before entering. As we know the heat of vaporisation of alcohol, we get the heat we could get out at A.

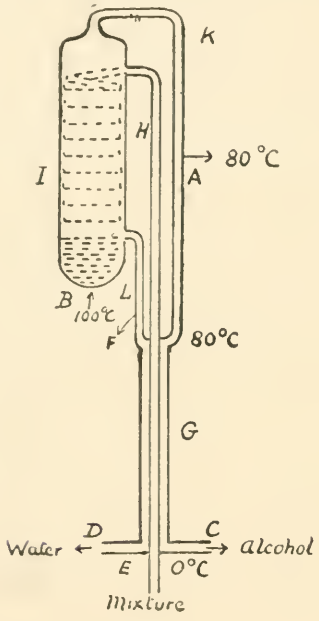


Fig I

Knowing the quantity of heating coming out, we know the heat put in at B. It might be thought that this would be anything the workman liked; this is not so, for if he put in too much, water would come out with the alcohol, and if too little, alcohol would come out with the water.

The broad result is that heat has to go in at 100° and come out almost wholly at 80°, the heat being roughly the heat of vaporisation of the most volatile liquid.

To see what happens when we do the separation by mechanical power we can imagine an ideal heat engine worked so as to deliver heat at 100° and to take in heat at 80°, or other temperature. If it does not get in enough at 80° it must make up the difference by direct degradation of work into heat, or better by taking in heat at 0°; if it gets in more than is wanted at 80°, it can deliver at 0°. If the process merely involved taking in the heat of evaporation of 500 grms. of alcohol at 100° and giving it out at 80°, calling the heat H, the engine would have to take in H353/373 at 80°, or 353° A, and by doing 20H/373 of mechanical work on the medium, H would be put into the rectifier at 100° C. The 20H/373 left over could be let down to 0, doing (353—273)/353 × 20H/373 = 0·0122H. Thus if the heat of vaporisation were 100, the first engine would do 5·36, and the other engine would recover 1·22, so that the total mechanical work to be done would be 4·15 of the heat of vaporisation of the alcohol, or 18,000 joules per minute, or 300 watts. Instead of adopting the rough statement that we have to supply the heat of vaporisation of the alcohol, we may work the example out approximately.

The alcohol vapour at K carries over 436,000 joules as compared with its liquid state at the same temperature. This is not all given out at A, because a little is wanted for the interchanger G. This has mixture coming in, being heated from 0° C. to 80° C., and 500 grms. of water and 500 of liquid alcohol both at 80° C. will not heat it, as the specific heat of the mixture is higher than the mean of the components. This is to be expected, because equal parts of alcohol and water give out 29,000 joules per kilogrm. on being mixed, so the disgregation energy of the mixture must be greater, and the heat taken in between 0° and 80° is largely disgregation energy. The extra heat needed is about 34,800 joules. This is returned to the rectifier by the hot mixture, so we get out 436,000 – 34,800 = 401,200 joules at A. We also get 42,000 by the water coming out

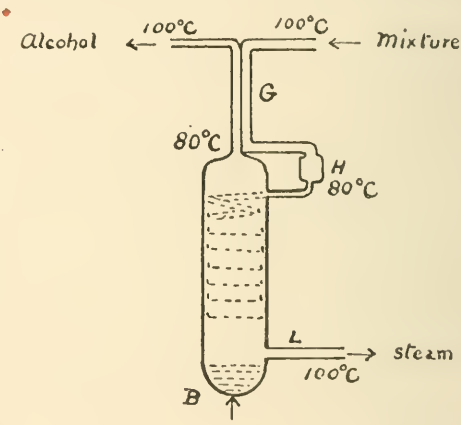


Fig 2.

at L at 100° C. and being cooled to 80° C. before entering the exchanger G. We thus have to supply 443,200 joules at 100° C. at B.

The heat of the water in L may be utilised. The difference of entropy of 500 grms. between 100° C. and 80° C. is 116·5 in practical units, so the heat put in at 100° C. is 373 × 116·5 = 43,500 joules; of which 42,000 are from the heat of the water and 1500 from work done. This leaves 399,700 to be supplied by an ideal engine working between A at 80° C. and B at 100° C. Such an engine will take in 378,280 as heat and put in 21,420 as work. But there are 401,200 joules coming out at A, so there is a balance of 22,920. An engine working between A at 80° and 0° C. will utilise 7820 joules out of this, rejecting 15,100 at 0° C. We thus have 1500 + 21,420 – 7820 = 15,100 joules to put in mechanically, or 252 watts.

One of the chief difficulties in this sort of calculation is the uncertainty as to the numerical data. This case is also complicated by the internal energy of the alcohol and water separate being greater than that of the mixture.

To get rid of the effect of the internal energy of the separated liquids in the last case the arrangement shown in Fig. 2 may be discussed. Here mixed alcohol and water as vapour comes in at 0. It goes to an interchanger G, where it is cooled down to 80° C., being thus condensed,

and it flows by the pipe H to the rectifier, which is as before, except that it gives out steam at L instead of water. The alcohol coming out at K is taken away as vapour. The mixed vapours condensing in G will give off much more heat than is necessary to raise the alcohol vapour from 80° C. to 100° C., so heat will be given off along G. For want of data as to heat of vaporisation of mixtures of alcohol and water I have taken the heat that would be given out by 500 grms. of each and deducted the extra internal energy, 29,000. This gives 1,541,550 joules given out along G, after deducting 950 for heating the issuing alcohol vapour. We must therefore supply this at 100° C. at B. As this large amount of heat is given off all along G it is difficult to know its value. To get it we would need a table giving the boiling-points of the range of mixtures of alcohol and water, and the composition of the vapour coming off, and to be quite accurate we should have a column of heats of vaporisation. For simplicity we shall not be far wrong if we take the heat as being given out at 94° C. This needs 25,200 joules given mechanically and 1,541,550 taken in as heat from G. Another engine will have to put in 1120 joules as work, taking in heat at 0° and giving out 3805 at 100° C. We have thus 26,320 joules per minute or 438 watts. This figure is most likely rather inaccurate, as the data are doubtful. The example is complicated by the heat of combination of alcohol and water too. Broadly speaking, what has to be done is to put in heat at the boiling-point of the less volatile liquid, taking out heat at a temperature between it and the boiling-point of the more volatile liquid. This involves either supplying the system with heat at one temperature and recovering some of it at a lower temperature or supplying energy mechanically.

The case of separating oxygen and nitrogen is simpler, as there is no development of heat on mixing the gases. It is exceedingly unlikely that there is any liberation of heat on mixing the liquids, but in the ideal case discussed next, if there were such heat it would not affect the reasoning, as its influence would cancel out.

Suppose for simplicity we are operating, say in Dis, at a temperature of 90° A., and we have a system as shown

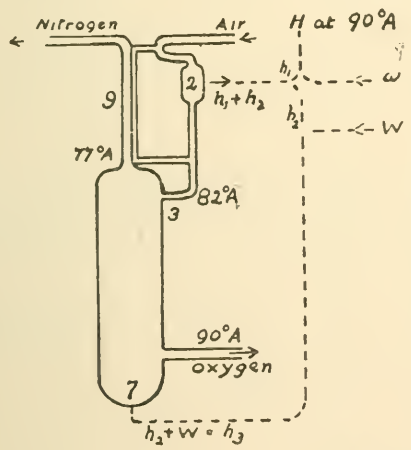


Fig 3.

with a pipe leading in air at 90° A., and two pipes delivering oxygen and nitrogen at 90° A.

Air comes in at A and the pipe branches, most of the air going to the cooler 2, where it is reduced to say 82° A., a good deal being liquefied. The partly condensed air then goes into the rectifier at 3. Nitrogen comes out as gas at 4, at 77° A., and is raised to 90° A by a portion of the entering air going down the interchanger 9. Heat has to be supplied to the rectifier at 7 to boil off the oxygen, and heat is given out at 2. Thermodynamic engines take in heat from 2, and deliver some of it at 7 and the rest to the outside. We have to find the power necessary to drive the engine to separate a kilo of air per minute, or the energy to separate a kilo of air. A kilo of separated air in an ideal engine with semipermeable pistons could do 13,180 joules in allowing the gases to mix at 90° A. 13,180 joules must therefore be done in separating them. As the internal energy of the separated gases is the same as that of the mixture, this work must be wholly degraded into heat. The system that takes in air and gives out oxygen and nitrogen at the same temperature and pressure must therefore give out heat, taking in work; and the heat for each kilo of air is thus 13,180 joules.

We do not really need to trouble ourselves as to what goes on inside our closed system. We do not need to know anything about the heat of vaporisation, boiling-points, or heat of mixture; all we have to know is the work that can be imagined as obtainable by a suitable arrangement for mixing the gases, and we then know the mechanical energy ideally necessary to separate them, assuming the system to have no irreversible process going on inside.

But it is worth while to look inside.

Call the heat given out at 90° A., H, and 90° A., h_1 and the temperature of 2, θ_2. Let the heat H be given out by a thermodynamic engine taking in work w_1 and heat h_1 from 2 at θ_2. Then H is made up of $h_1 + w_1$, and $h_1 = H\theta_2/\theta_1$, and $w = H(\theta_1 - \theta_2)/\theta_1$. The rest of the heat given out at 2 is taken in by a second thermodynamic engine at θ_2 and given to the rectifier at θ_1. Call this heat h_2, then the heat given to the rectifier is $h_2\theta_1/\theta_2$ and the work done by the second engine, W, is $h_2'\theta_1 - \theta_2)/\theta_2$. But $H = W + w$ and $h_1 + h_2 = h_3$, as the rectifier takes in and gives out the same amount of heat. From these equations we get $w = H(\theta_1 - \theta_2)/\theta_1$, and $W = H\theta_2/\theta_1$.

Suppose that instead of working at 90° we lead the inlet and two outlet pipes through an interchanger, and work at 273° A., or say 270° A. to make a round number. The work W is not altered, as the conditions of that engine are not interfered with; but the first engine that takes in hea h_1 at θ_2 now has to give it out at 270° A. instead of 90° A. It is simpler arithmetically to imagine a third engine taking in the heat H at 90° A. and giving it out at 270° A. This engine does 2H.

It is hardly necessary to repeat that the mechanical power needed varies as the absolute temperature, as the work ideally obtainable on mixing the oxygen and nitrogen at atmospheric pressure varies as the absolute temperature.

Take now the case of dry air to be separated completely into oxygen and nitrogen. The work ideally obtainable from a kilogrm. of the gases mixing is 40,000 joules, so to separate a kilogrm. a minute needs 666 watts in a perfect machine where all the processes are reversible. This would come out fairly expensive on a very large scale.

In this case it has been assumed that the air is to be separated completely into pure oxygen and pure nitrogen. It does not follow that it pays to separate in this way unless both gases are wanted pure in the proportion of four to one. If oxygen alone is wanted, it does not pay to make pure nitrogen, for that means abstracting oxygen from a mixture with very little oxygen, while air is obtainable at no cost. To separate a kilogrm. of air at 0° C. into pure oxygen and nitrogen needs 40,000 joules to be converted into heat;* to take out half the oxygen needs only 17,000 joules, but as this gives only 115 grms. of oxygen 34,000 joules are needed to give the same weight of oxygen. If the oxygen is wanted for enriching air for combustion purposes, it is cheaper to extract it impure. But for pure oxygen the most economical proportion to

* For simplicity atmospheric pressure is taken as a megadyne per sq cm.; and heat is taken in joules, not calories; entropy, where necessary, can be taken in entrops, which, multiplied by the lowest available temperature, give the incurred waste in joules.

extract—on paper—is about 50 per cent. In practice it may be better to take out a little more, as the less gas you pass through the apparatus the smaller it may be.

It might be said that given a kilogrm. of air cooled down, a machine that extracts all the oxygen does its work better and is cheaper; this is not the case, however, as air does not cost anything appreciable, even cooled.

We have therefore the problem of taking in heat at a temperature of about 82° A. and giving it out at 90° A. and the temperature of the room, say 290° A.

There are broadly two methods in use. It is not necessary to trace the history of the liquefaction of gases, and to follow out the ingenious intensification methods. They are all well described in the literature of the subject. (The engineer will find "Air Liquide," G. Claude, and "The Mechanical Production of Cold," Ewing, interesting).

The first method is Linde's. This takes advantage of the discovery by Kelvin and Joule that such gases as air have less internal energy when compressed. If you feed a heat-insulated system with air under compression and let it expand before it comes out, the air coming out must at first take out more energy than the air going in carries with it; so the inside of the apparatus must get colder and colder. If the outcoming air comes through an interchanger it will come out at the same temperature as the ingoing air, so the other end of the apparatus must get colder and colder until some of the air is liquefied. The balance will come when the internal energy of the gas and liquid air taken out is equal to that of the compressed air going in.

In practice the same machine does the liquefaction and separation; but it is simpler for our purpose to treat a machine in which air is compressed and allowed to expand as a thermodynamic engine, using the liquid air as a means of extracting heat at a low temperature. It was this invention of Linde's that made the production of liquid air, and his subsequent invention of combining the rectifier with it that made the commercial production of oxygen thermodynamically from air possible.

The other invention is due to Claude. It was of course obvious that cold could be produced by comprsssing the air at a high temperature and then expanding it so as to do external work to a low temperature, and the merit does not here lie in the idea. But to work out such a system is a very different matter. The practical difficulties in making an engine that would give out any reasonable power at a temperature of 80° A. are very serious indeed.

(To be continued).

BASIC NITRATE OF YTTRIUM.

By C. JAMES and L. A. PRATT.

Of all the methods that have been published for the separation of yttrium and erbium, the classic procedure of Bahr and Bunsen still serves best (*Ann.*, 1866, cxxxvii., 1). It was therefore considered that a study of the system Y_2O_3,N_2O_5,H_2O would be highly interesting.

The only basic nitrate mentioned by Bahr and Bunsen was given the formula (re-calculated) $2Y_2O_3 \cdot 3N_2O_5 \cdot 9H_2O$, which was derived from the analysis of the air-dried salt. It is highly probable that their compound was contaminated with normal nitrate from adherent mother-liquor.

In order to study the system Y_2O_3,N_2O_5,H_2O it was necessary to prepare a comparatively large amount of pure yttrium oxide, since yttrium nitrate is extremely soluble.

The Preparation of Yttria Material.

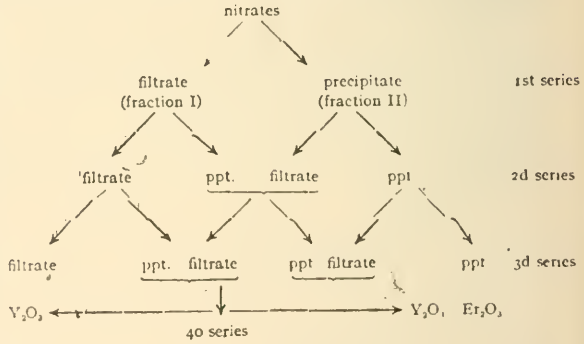
The crude yttria earths were first submitted to a long fractional crystallisation by the bromate method (*Journ. Am. Chem. Soc.*, xxx., 182). By this procedure samarium, gadolinium, terbium, dysprosium, and holmium separated in the least soluble portions. The middle fractions contained yttrium, together with a little erbium and holmium, while the most soluble portion carried nearly all the erbium and all the thulium, ytterbium, lutecium, and scandium.

The middle fractions were then precipitated as the hydroxide, and well washed with boiling water. The hydroxides were next converted into the nitrates, and the latter subjected to fractional decomposition. This was carried out by evaporating the solution and fusing until a portion had decomposed. The evolution of red fumes was allowed to proceed until the surface acquired a peculiar steely appearance. This point was easily ascertained by experience. The decomposition was not allowed to continue until the mass became creamy.

In order to find the best method of obtaining the solution of the melt, several plans were tried. It was discovered that the simplest way was to pour the fused mass into cold water. Great care was required in order to prevent spattering. The result of this operation was a nicely granulated product, which rapidly disintegrated upon boiling.

Under the best conditions the entire mass went into solution; especially was this true of the yttrium end of the series. Upon cooling, the basic nitrates separated out in a crystalline form. At the opposite end—the least basic portion—of the fractions there always remained an insoluble basic nitrate, unless the decomposition was stopped at an earlier stage, *i.e.*, when there was a copious evolution of red fumes.

In case a precipitate remained, it was highly important that it should be well agitated by thorough boiling. After cooling, the precipitate was filtered off (Fraction II.), re-dissolved in nitric acid, and again fused. The filtrate



Fraction I.) was also boiled down, and fused. This second series gives two filtrates and two precipitates. The filtrate from Fraction II. was mixed with the precipitate from Fraction I., with the result that the second series contained three fractions. The diagram will readily show the manner in which the work was carried out.

About forty series of operations were carried out, yielding 2 kilos of yttrium nitrate. The nitrate was dissolved in water, heated, and precipitated by means of oxalic acid. The resulting oxalate was filtered off, well washed, dried, and ignited.

The white oxide obtained in this way was dissolved in excess of nitric acid, and twice crystallised from this solvent.

A saturated solution of the nitrate was then prepared by using 1 kilogrm. of the salt. The spectroscope showed only very faint bands of erbium and holmium when viewed through a layer 12·5 cm. thick, and the solution was perfectly colourless. Therefore it was considered sufficiently pure for the study of the basic nitrates.

Some of the remaining fractions of yttrium, which still contained a little erbium and holmium, were put through a modified chromate method. This yielded a further supply of yttrium oxide of such a purity that, when converted into a concentrated solution of the nitrate, it showed no absorption bands through a layer of about 5 cm.

Twenty-two solutions were prepared, in regularly increasing concentrations of yttrium nitrate, from great dilution to a saturated solution. These solutions together with an excess of yttrium oxide were placed in bottles of 100 cc. capacity, and rotated in a thermostat at 25°. After an interval of three months, several of the solutions were analysed. During the analysis, it was observed that the solid phase in those solutions having a fairly high concentration of yttrium nitrate was composed of fine crystals. These bottles cleared in a comparatively short time, so that the supernatant liquid could be readily drawn off. In the bottles where the concentrations were not so great the solid phases settled with difficulty, and had more the appearance of a hydroxide. After four and a-half months of rotation, the system was found to be in equilibrium. The solutions were withdrawn, and the yttrium, present as the hydroxide, and the total yttrium determined.

Several difficulties were encountered in carrying out these analyses, and different methods were tried in order to reduce errors to a minimum. The following methods gave the most accurate and rapid results :—

A weighed amount of mother-liquor was, after considerable dilution, titrated to the neutral point with standard nitric acid (approximately one-tenth normal), using methyl-orange as the indicator. From this, the amount of yttrium oxide, present as hydroxide, was easily calculated. Checks, which were run on several of the solutions, proved that dependence could be placed upon the results obtained.

In order to determine the total yttrium, the solutions, which had previously been titrated, were diluted to 200 cc. Aliquot portions of these diluted solutions were warmed, and treated with a slight excess of an oxalic acid solution. After being allowed to stand for some time, the precipitate was filtered off, dried, and carefully ignited to the oxide in a weighed platinum crucible.

The data obtained from the analyses of the solutions are given in Table I., and shown graphically in Fig. 1.

Table I.

No.	Density 25°/25°.	Y_2O_3 as $Y(NO_3)_3$. Per cent.	Y_2O_3 as $Y(OH)_3$. Per cent.	$Y(NO_3)_3$ in 100 grms. H_2O. Grms.	Y_2O_3 as $Y(OH)_3$ in 100 grms. H_2O. Grm.
1.	1·0260	1·25	0·014	3·13	0·014
2.	1·0675	3·17	0·021	8·37	0·022
3.	1·1106	5·01	0·033	13·87	0·034
4.	1·1506	6·57	0·039	19·05	0·048
5.	1·1907	8·20	0·049	24·94	0·063
6.	1·2350	9·58	0·071	30·46	0·091
7.	1·2517	10·19	0·121	33·02	0·160
8.	1·2897	11·45	0·088	38·71	0·122
9.	1·3268	12·61	0·079	44·35	0·114
10.	1·3698	14·02	0·068	51·87	0·103
11.	1·4104	15·17	0·060	58·61	0·095
12.	1·4484	16·31	0·054	65·89	0·090
13.	1·4867	17·33	0·045	73·03	0·078
14.	1·5231	18·33	0·039	80·67	0·072
15.	1·5587	19·34	0·039	89·06	0·074
16.	1·5923	20·10	0·038	95·98	0·074
17.	1·6259	20·91	0·037	103·80	0·075
18.	1·6603	21·82	0·037	113·40	0·079
19.	1·6931	22·59	0·036	122·40	0·080
20.	1·7260	23·37	0·032(*a*)	132·10	0·074
21.	1·7440	23·74	0·035	137·10	0·083
22.	1·7446	24·07	—	141·60	—

(*a*) This result undoubtedly contains a slight error, but. unfortunately, the bottle was emptied before it could be checked.

Bottle No. 21 contained an excess of both basic yttrium nitrate and yttrium nitrate. Bottle No. 22 contained only an excess of yttrium nitrate, which gave for the solubility of this compound at 25° 141·6 grms. per 100 grms. of water.

For the analysis of the solid phase, the sample was withdrawn, freed as far as possible from adhering mother-liquor, by pressing between filter-paper, after which it was quickly transferred to a weighing bottle and carefully mixed. A known amount was then ignited in a weighed platinum crucible for total yttrium. In another portion of the same sample the yttrium oxide as yttrium hydroxide was estimated by dissolving a weighed amount in an excess of standard nitric acid, and titrating back to neutrality with a sodium carbonate solution of known ratio. In this case methyl-orange was again used as the indicator.

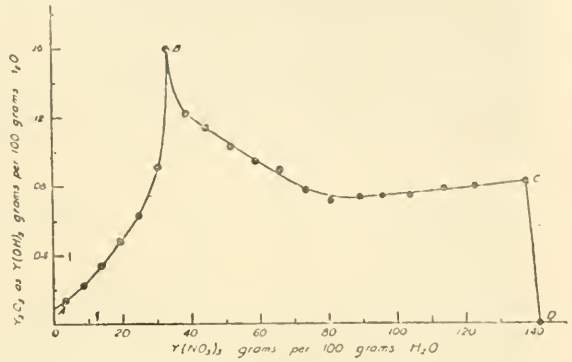


Fig. 1.

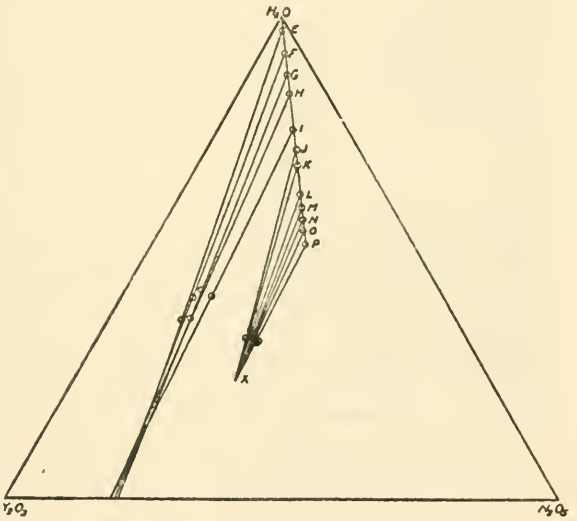


Fig. 2.

The results are given in Table II., and plotted on the triangular diagram in Fig. 2.

Table II.

Point.	Solutions. Y_2O_3.	Solutions. N_2O_5.	Point.	Solids. Y_2O_3.	Solids. N_2O_5.	Bottle No.
E ..	1·26	1·79	E′ ..	49·55	13·29	1
F ..	3·19	4·55	F′ ..	45·20	12·96	2
G ..	5·04	7·18	G′ ..	42·97	13·74	3
H ..	6·61	9·42	H′ ..	47·82	14·56	4
I ..	9·65	13·74	I′ ..	41·67	16·22	6
J ..	11·54	16·42	J′ ..	39·78	26·98	8
K ..	12·69	18·08	K′ ..	38·09	26·93	9
L ..	15·23	21·75	L′ ..	38·21	27·89	11
M ..	16·36	23·39	M′ ..	38·39	28·12	12
N ..	17·38	24·83	N′ ..	38·19	28·70	13
O ..	18·37	26·28	O′ ..	38·44	29·19	14
P ..	19·38	27·73	P′ ..	37·83	29·58	15

It will be seen that the lines (EE', FF', and GG', &c., of Fig. 2) joining points represented on curve A B of Fig. 1 do not intersect at a common point; also the solids, upon examination, showed a great resemblance to yttrium hydroxide. Therefore the precipitates along this line can only be solid solutions. Lines joining any points along the curve B C (Fig. 1) meet at a common point x, which corresponds to a definite hydrated basic nitrate of yttrium possessing the formula $3Y_2O_3.4N_2O_5.20H_2O$.

The basic nitrate consisted entirely of small crystals, which were rapidly decomposed by water. The compound, however, was not affected by continued washing with absolute alcohol, and, since the normal nitrate is very soluble in this liquid, it could be entirely separated from the basic nitrate. The solids from several bottles along the curve B C were filtered upon a Hirsch funnel, washed with absolute alcohol, air-dried, and analysed. The results obtained were as follows:—

	Y_2O_3.	N_2O_5.	H_2O.	
Calculated	46·10	29·40	24·50	
Found (bottle 10) ..	46·09	29·55	24·36	(diff.)
Found (bottle 11) ..	45·96	29·67	24·37	,,
Found (bottle 13) ..	45·82	29·67	24·51	,,

The basic compound from still another bottle was dissolved in yttrium nitrate solution, and re-crystallised after filtering. The mother-liquor was separated by suction, the crystals washed with absolute alcohol, and air-dried. The analytical results obtained agreed well with the above as may be seen:—

Y_2O_3	45·82
N_2O_5	29·67
H_2O	24·51

For this compound the authors offer the following complex formula:—

$$(NO_3)_2Y{-}O{-}Y{-}O{-}Y{-}O{-}Y{-}O{-}Y{-}O{-}Y(NO_3)_2 + 20H_2O$$
$$\qquad\quad |\qquad\quad |\qquad\quad |\qquad\quad |$$
$$\qquad NO_3 \quad NO_3 \quad NO_3 \quad NO_3$$

From the foregoing work the following conclusions are drawn:—

First, that the basic compound mentioned by Bahr and Bunsen does not exist. Their results were undoubtedly due to adherent normal nitrate.

Secondly, the only basic nitrate that does exist at 25° is the one corresponding to the formula $3Y_2O_3.4N_2O_5.20H_2O$.

Thirdly, this compound is stable in air, and can exist in contact with water containing more than 33 grms. of yttrium nitrate to 100 grms. of water.—*Journal of the American Chemical Society*, xxxii., No. 7.

THE DETERMINATION OF LEAD IN NON-FERROUS ALLOYS.*

By C. P. KARR.

THE use of lead in the foundry goes back to the remotest period of human industry. Its general properties are well known, and when by intent or carelessness they are violated, the founder soon discovers his mistake without much difficulty; its application within very narrow limits is well understood by all practical metal workers. So important a factor has lead become in every foundry where a diversified range of castings is made that it has been deemed necessary to determine the percentage of that element in any form of alloy in which lead may be present. To accomplish this end chemists have made exhaustive researches to discover assay methods that should be accurate, easily conducted, and conclusive. In this paper the methods of assay referred to apply to the alloys into which lead enters in the course of foundry practice rather than to the ores in which lead occurs.

* A Paper read before the American Brass Founders' Association. From the *Chemical Engineer*, xii., No. 6.

Gravimetric Methods.

Alloys not containing tin may be proceeded with directly for the determination of lead, but if tin be present the alloy is dissolved in nitric acid, evaporated to dryness on the water-bath, diluted, allowed to settle, filtered, and the filtrate treated with 2 to 3 cc. of H_2SO_4, evaporated until fumes of SO_3 are driven off, cooled, diluted with 20 to 30 cc. of water, washed with dilute H_2SO_4 or alcohol, or both, dried in the steam-bath, precipitate detached from the filter, the paper and the precipitate ignited separately, their ashes united, a drop of nitro-sulphuric acid added, gently dried, and re-ignited and weighed as $PbSO_4$, or the precipitate is filtered through a Gooch crucible and dried at 105° C. to constant weight.

This method is very old, but is reliable only in the most skilful hands. In the incineration of the paper-filter there are two sources of loss, the oxidation and volatilisation of lead, and the difficulty of re-converting every particle of the lead reduced by the carbon of the filter back to the form of a sulphate. To overcome these difficulties the Gooch crucible is resorted to. Dr. Bollenbach (*Zeit. Ann. Chem.*, 1908, p. 690), states, however, that this sulphate reaction is not very convincing because the precipitate is soluble in strong nitric acid, and he proposed the precipitation of lead as a peroxide in an ammoniacal solution by means of bismuth, and gives his method in detail. In his paper on the volumetric assay of lead Dr. J. F. Sacher (*Chem. Ztg.*, Dec. 2, 1909, p. 1257) states that the precipitation of lead as lead molybdate offers an advantage over that of the sulphate method, as the molybdate salt is less soluble in water than the sulphate. In a nitrate solution of an alloy not containing arsenic, arsenates, nor phosphoric acid, ammonium molybdate may be used directly as a reagent for the quantitative separation of lead. Jannasch (*Ber.*, xxvi., 2329) has proposed a gravimetric separation of lead and copper from a nitrate solution by means of the hydrogen peroxide method, of lead from tin and zinc, metals which are of vital importance, and while these methods are of great importance to the research chemist, they are, on account of the difficulties incurred in the ignition for weighing, of limited use in the everyday routine of the foundry.

About the best example that can be offered of the importance of the gravimetric method is that of the determination of lead in babbit metal by Messrs. Walker and Whitman (*Journ. Ind. and Eng. Chem.*, August, 1909). Dissolve ½ to 1 grm. of alloy in a 250 cc. beaker with 20 cc. HCl, $5H_2O$, and add HNO_3 a little at a time until the sample is in complete solution. Evaporate to dryness on a steam-bath, add 5 cc. strong HCl (if sample contains 10 per cent or more lead add 10 cc. HCl), warm a few minutes, stir in 150 cc. of 95 per cent alcohol, allow to stand at room temperature for two hours, filter through a Gooch crucible, wash with about 100 cc. of 95 per cent alcohol, dry crucible in air-bath for one hour at 105° C. Weigh as PbO_2, add 0·0085 grm. to the weight of the precipitate, and multiply by 0·74473 to find the weight of metallic lead.

Volumetric Methods.

Numerous methods have been proposed for this determination; the three most prominent are Alexander's molybdic acid method, as modified by Low, the ferrocyanide method, and the permanganate method.

Alexander's original paper was first published in *Berg- u. Huttenm. Ztg.*, 1893, p. 201; Low's modification in *Journ. Am. Chem. Soc.*, xv., 550. He employs a solution of 4·25 grms. of the salt to the litre, which if ½ grm. be weighed out for the assay corresponds 1 cc. to 1 per cent of lead. Dissolve 0·2 grm. of pure lead in HNO_3, evaporate with H_2SO_4, filter off the lead sulphate, and wash with dilute H_2SO_4. The sulphate is decomposed with 25 cc. strong HCl, add 15 cc. HCl and 25 cc. water, and saturate with 25 cc. strong ammonia (sp. gr. 0·90). Finally, acidify with strong acetic acid, dilute with 200 cc. of water, heat to ebullition, and titrate.

The ferro-cyanide method is carried out with a lead acetate solution acidified with acetic acid, and titrate with a ferro-cyanide solution which contains 10 grms. of this salt to the litre. One cc. of solution for a 1 grm. assay corresponds to about 1 per cent of lead. Titrate till a drop taken out with a drop of saturated uranium acetate solution gives a characteristic brown colouring upon a porcelain plate. Low digests the lead sulphate with saturated ammonium carbonate solution to convert the sulphate into a carbonate, cools, filters, and dissolves the carbonate in a mixture of 5 cc. concentrated acetic acid and 25 cc. water, dilutes 100 cm. water, and titrates. If Sb or Bi are present then the lead sulphate is first of all treated with 10 cc. H_2SO_4 (1 : 1) and 2 grms. of Rochelle salts, add 40 cc. water, and boil. Dr. Bollenbach's method is a modification of the permanganate method (*Zeit. Anal. Chem.*, 1907, p. 582), but his method is a reversal of all former procedure. In a hot solution of potassium permanganate he adds the lead solution, made alkaline by NaOH, drop by drop to complete discoloration, adds some barium sulphate to facilitate the titration ; but his method has recently been studied by Dr. J. F. Sacher, who states that the behaviour of $BaSO_4$ towards $KMnO_4$ is completely indifferent, and that the method proposed is unreliable. Dr. Sacher advocates the adoption of the molybdate method (*Chem. Ztg.*, December 2, 1909, p. 1257), which he modifies as follows:—To conduct the titration there is required an ammonium molybdate solution of which 1 cc. corresponds to 0·01 grm. Pb and a 3 per cent tannin solution.

In addition there should be a lead nitrate solution containing 16 grms. of $Pb(NO_3)_2$ in water to the litre, of which 1 cc. corresponds exactly to 0·01 grm, of Pb, and ready for the back titration when necessary. With this solution the rest of the molybdate titration may be quickly controlled. The tannin solution must be freshly prepared, as it is not unalterable, a 2 per cent addition of acetic acid will prolong its sensitiveness toward the molybdate solution for one week; alcoholic tannin is more permanent, and is suitable as an indicator.

Applied to a bronze alloy, for example, the procedure would be to dissolve about 0·5 grm. in from 4 to 5 cc. of HNO_3 (sp. gr. 1·42), evaporate to dryness, dilute with water in the usual way, filter off the metastannic acid, precipitate the copper with the electric current or as a sulphocyanate, and determine the lead in the filtrate from the neutralised nitrate solution. Add 5 cc. ammonia, dilute to 100 cc. with hot water, allow to stand on water-bath two to three minutes, add 5 cc. of 80 per cent acetic acid, and titrate hot with ammonium molybdate. The volume of the titrated fluid is carefully measured, and the excess in molybdate corresponding to this volume, which occasioned the first yellow colouring with the tannin solution, is deducted from the cc. of molybdate solution found. A concentration below 0·15 per cent Pb is to be avoided, because such a condition makes the end-point indistinct.

In such a case the colorimetric method is preferable. The best results are obtained if the precipitate is allowed to settle on the water-bath from two to three hours. To be filtered cold, wash with water till the filtrate shows no more turbidity with the neutral lead solution, dry at 100° C., ignite gently after separate incineration of the filter, and weigh after cooling as $PbMoO_4$. A large percentage of iron in the alloy interferes with an accurate result. This may be avoided by precipitating the excess of iron as a hydroxide in the presence of acetic acid.

A new and simple volumetric method has recently been proposed by Dr. Rupp (*Chem. Ztg.*, Feb. 8, 1910, p. 121), as follows :—Twenty or 25 cc. of a half normal solution of potassium cyanide is rinsed into a 100 cc. flask, mixed with a suitable volume of lead solution (1 to 5 per cent) free from acid. Fill up to the mark, mix thoroughly, filter after five to ten minutes, and titrate 50 to 75 cc. of the filter with quarter to half normal acid to determine the excess of alkaline cyanide. Use methyl-orange as an indicator. If the lead salt solution contains any acid in a free state it is made exactly neutral with dilute NaOH in presence of methyl-orange. The foundation equation is $2Cy + Pb'' = PbCy_2$. The calculation is as follows :—

1 Pb = 2 KCy = 2 HCl and 0·05178 grm. Pb = 1 cm. N/2 KCy = 1 cc. N/2 HCl.

The cyanide solution may be standardised against a pure metallic lead or pure metallic copper in the usual way, using 98 to 99 per cent pure potassium cyanide. The accuracy of the method is ensured by the absence of free acid in the lead solution. For an alloy containing a small amount of lead, say, less than 0·15 per cent, the colorimetric method has no rival for accuracy, neatness, and dispatch. Iron, however, in the ferric state introduces an inaccuracy. The solution should be dilute neutral and a nitrate. The method is based upon the comparative colour intensity of two liquids of the same concentration and volume, of an unknown with a known value. This analysis may take place in one of two ways :—A known solution of a definite volume and known concentration may be compared with an unknown solution having the same volume, and, if it have the same concentration, it will have the same depth or tint of colour that the known solution exhibits. With coloured fluids that are stable a series of concentrated solutions may be kept in readiness as a basis of comparison. In the second method, use is made of the fact that two solutions of different volume densities appear to be equally coloured if their concentration is inversely proportional to the intensity of their colour. In a special colorimetric apparatus the height of the column of the liquid is altered until both have the same intensity of colour, and calculate the desired concentration from the proportion of the depth of the two columns.

Method.—Mix the given lead solution with an excess of sulphide solution, and select from a series of similarly treated comparative solutions of various but of known constitution which has been previously prepared from a pure lead nitrate, the one which appears to have the same colour for the same volume. Its concentration will be the same as that of the solution which is being tested.

Execution.—Use a colorimetric apparatus if possible. Dry at 120° a re-crystallised sample of purest merchantable lead nitrate, weigh out 0·0160 grm. of it, and dissolve in a measuring flask. Dilute to 1 litre. With the solution (A) containing 0·01 mgrm. of Pb per cc., fill up a burette. In graduated cylinders put 40, 30, 20, and 10 cc. of this fluid, dilute each to 50 cc. Prepare in addition four other solutions (B, C, D, and E), which contain 0·008, 0·006, 0·004, and 0·002 m.grm. of lead per cc. In one of ten about equally wide and high reagent glasses place upon a label a mark removed about 3 cc. from the edge, and indicate exactly the same (measured from the bottom) height in the same way, in the rest of the nine glasses. Fill up No. 1 with the lead solution to be tested; Nos. 2 to 6 with the comparison solutions A, B, C, D, and E. Fill up No. 7 with pure distilled water to the mark. Now, in each of the seven glasses add from 3 to 4 drops of colourless (*i.e.*, 10 per cent) ammonium or natrium sulphide solution, shake or stir the fluids thoroughly, compare the colours. In making the comparison hold or place the two vessels against a background of opaque white glass. The examination should take place in a diffused light of uniform illumination. As soon as it is established between which of the concentrations the unknown lead solution lies, then prepare three additional comparison solutions of intermediate concentration, so that the lead constituent of one to the other bears the relation of about 0·0005. Pour this into reagent glasses Nos. 8, 9, and 10, and compare them likewise with the solution of unknown strength. Set their colours (for example, between those of C and D, *i.e.*, 0·006 and 0·004 mgrm. per cc.); thus the new solutions have 0·0055, 0·0050, and 0·0045 mgrm. per cc. Therefore the 27·5, 25, and 22·5 cc. of the solution A are to be diluted up to 50 cc. Repeat this until constant results are obtained; the concentration up to 0·0005 mgrm. of Pb is exactly determined.

If the lead constituent in the given solution rises above

0·01 mgrm. per cc., then the sulphide addition causes too great a darkening for the comparison, and the fluid is correspondingly diluted. Mgrms. of lead should be expressed in cc. Woudstra (*Zeit. Anorg. Chem.*, lviii., 168) states that the method by H_2S is inexact in the presence of Fe. In the *Journ. Soc. Chem. Ind.* (Jan. 15, 1910, p. 7) J. M. Wilkie takes exception to the use of a sulphide salt alone as a source of colour comparison; he prefers to add a solution of KCy or hydrocyanic acid to the lead solution previously made alkaline with ammonia. Iron present must be in a ferrous state, and ferrous hydroxide must be precipitated under conditions that ensure its intimate contact with KCy. Sodium sulphite is used as a reducing agent. The solution to be tested must be colourless before the alkaline sulphite is added. If the solution to be treated is not acid it is to be acidulated with a few drops of acetic or other acid to a distinctly acid reaction, 1 cc. of a 10 per cent solution of KCy is then added, and finally a considerable excess of ammonia, if colourless add the sulphide. If the iron is present originally in the ferric state add a few drops of N/10 sodium thiosulphate, heat slowly to incipient boiling, allow to stand until the colour suddenly bleaches out, then add KCy and NH_4OH as usual.

Centrifugic Method.

In the *Chemiker Zeitung Repertorium* of Feb. 13, 1909, there was published an account of the "Centrifugic Method" used successfully by an Italian chemist in the works of Ansaldo, Armstrong, and Co., in Cornigliano, Liguria. According to the supposed lead constituent he weighs out from 0·5 to 5 grms. of the alloy to be tested, treat with HNO_3 in the same way as in a solution for the determination of lead sulphate, filter off the metastannic acid, evaporate the filtrate with H_2SO_4 until white fumes appear, cool, dilute with 20 cc. of water. Use a centrifugal apparatus. The tubes used are graduated somewhat similar to that of a burette. A certain factor dependent upon the weight taken is used in obtaining results. If 2 grms., for example, have been weighed out and the tube reading is at the twelfth division, then by multiplying this reading by the factor 0·2274 the lead content becomes 2·728 per cent of Pb.

Frank Castek (*Osterr. Zts. Berg- u. Huttenm.*, 1909, lvii., 665—684) uses a phosphorus centrifuge machine, and prefers the ammonium molybdate precipitation of lead to that of the sulphate. His conclusion is, that applied to ore containing less than 35 per cent, using 1 grm. for a determination, the results are concordant, but somewhat too high; 14 tests could be made in five hours.

Planimetric Method.

The planimetric method of assay of lead in non-ferrous alloys may safely be described as the latest to arrive among us. It is essentially a microphotographic method. In a non-ferrous alloy containing many ingredients it would be necessary to eliminate tin, copper, antimony, and arsenic in the usual manner, and reduce the alloy if possible to such a state as to contain but two metallic ingredients, preferably zinc and lead. Obtain a sulphate solution, evaporate to dryness until fumes of SO_3 escape, and transfer the same to a porcelain crucible, reduce and ignite to a prill or button of lead, allow to cool, remove the prill, flatten carefully, and etch with dilute nitric or sulphocyanic acid, and take an enlarged microphotograph of the same. Prepare several standard micrographs of lead-zinc alloys or lead alone, or lead and tin, or lead and copper, or lead and antimony, or lead and arsenic, with the planimeter in the usual way, measure the lead area shown by the microphotograph, and by the method of proportion compare the areas of lead in the unknown compound with the areas of the known compound. To anyone familiar with operating a planimeter the method becomes exceedingly fascinating, and if the buttons or prills of a known composition are carefully prepared and clearly photographed to scale, the results are accurate and conclusive. The percentage composition is arrived at in the usual way, viz:—The proportional area of the known composition is to the percentage of the ingredient known as the proportional area of the required ingredient measured by the planimeter is to its required percentage composition.

Electrolytic Method.

Lead is deposited from a strong nitric acid solution at the anode as PbO_2. To facilitate the deposition, the anode should revolve about 500 revolutions per minute. The current density should be about 5 ampères, and the terminal pressure between 3 and 4 volts; after ten minutes, interrupt the current for some seconds in order to accelerate the reduction of the metallic lead separating at the anode, and repeat this once again towards the close of the assay. After thirty minutes, test the solution for lead with ammonium sulphide. When the work is finished, shut off the current, dip the anode wire or gauze in hot water and then in alcohol, and dry for an hour at 230° and weigh.

The weight of the PbO_2 found multiplied by 0·866 according to H. J. S. Sand and E. F. Smith, by 0·8643 according to A. Staehler, but by 0·857 according to Hollard and Bertiaux. This discrepancy is due to differences of the thoroughness in the expulsion of the water from the deposit. The question has been carefully studied by H. J. S. Sand. He dried the deposits in a specially contrived drying oven where he could maintain a temperature almost constant between 230° and 240° C. It is my conviction that this empirical factor must be established by a series of experiments that apply to the oven itself and the conditions under which the assay is conducted. By igniting the PbO_2 to PbO as suggested by Treadwell, which can be done if a platinum dish be used as the anode, this difficulty of drying at a constant temperature may be overcome and with more accurate results. In conclusion, the writer would say that the last method is the best of all for rapid accurate work.

REPORT ON CHEMICAL CONSTITUTION AND THE ABSORPTION OF LIGHT.*

By W. W. STRONG.

A Method of Chemical Analysis.

RESEARCH along many lines in science is often very much stimulated by the requirements of technology. This is especially true in connection with many branches of organic chemistry, and a good example is furnished by the pure food laws. In regulating the use of various colouring and preserving matters added to foods, it is necessary that the examiners shall be able to recognise various compounds easily and quickly. Many organic compounds possess very characteristic colours, and it has often been asked whether the absorption spectra of these compounds would aid in their analysis. Our present knowledge of absorption spectra is mostly limited to the visible region of the spectrum. Before this method of analysis can reach its full service to chemists it will be necessary to measure the absorption throughout the region of the infra-red. At present the absorption spectra of a few potassium salts have been explored to regions of wave-lengths as long as 0·1 mm. (Electro-magnetic waves having wave-lengths between 8000 m. and 6 mm. have been produced).

The analysis of inorganic compounds is probably less hopeful, although the absorption spectra would often help to identify compounds. A great many of the inorganic cations show characteristic absorption in the visible portion

* This Report is based upon an article by H. Ley, entitled "Ueber die Beziehung Zwischen Lichtabsorption und Chemischer Konstitution bei Organischen Verbindungen." See *Jahrbuch der Radioaktivität und Elektronik*, 1910, vi., 274. From the *American Chemical Journal*, xliv., No. 1.

of the spectrum and practically all have bands in the infra-red. J. Formanek has suggested that the presence of metals in metallic compounds of alkannin could be determined from the absorption spectra of these compounds ("Die Qualitative Spectralanalyse Anorganischer Körper"). The following measurements of the absorption bands of the different compounds of alkannin show the effect of the metal upon the position of the bands :—

	λ.	λ.	λ.
Uranium	6870	6315	—
Iron	6545	6030	—
Potassium	6387	5910	—
Cobalt	6370	5845	5405
Sodium	6337	5857	—
Barium	6281	5805	5395
Lithium	6210	5745	5340
Nickel	6192	5725	5320
Calcium	6147	5682	5276
Copper	5953	5515	5128
Aluminium	5857	5425	5048

The use of absorption and emission spectra has been very successful in studying the elements of the rare earths, and has been very extensively applied by Crookes, Becquerel, Exner, Demarçay, and many others. An account of this work is given by Böhm ("Die Darstellung der Seltenen Erden," Leipzig, 1905). Recently, Urbain ("Le Radium," June, 1909) has employed the phosphorescent spectra in the purification of compounds of europium, gadolinium, terbium, dysprosium, neoytterbium, and lutecium.

Atomic Structure and Spectra.

The greatest interest lies, however, in the relation between chemical constitution and absorption or emission spectra. The relation between flame, spark, and arc spectra and the chemistry of the emitters is not known. The source of spectra like that from the blue cone of a Bunsen burner, the Swan spectra, is at present a much mooted problem. It is probable that chemical reactions play an important *rôle* in the emission and absorption of spectra, and especially of band spectra. We usually think of most spectrum lines like D_1 and D_2 of sodium as coming from the metallic atoms. Fredenhagen points out that under most conditions oxygen is present (*Phys. Zeit.*, Oct. 24, 1907). In chlorine, hydrogen, or fluorine flames, calcium, strontium, thallium, sodium, barium, and copper emit spectra that are very different from those obtained when oxygen is present. Under these conditions thallium does not emit the characteristic green line and the lines D_1 and D_2 are completely absent. Work on the absorption of sodium, mercury, potassium, and various other vapours show that the presence of foreign gases modifies the character of the absorption very much. Many believe that certain series or groups of lines are due to chemical reactions of various kinds.

Chemical reactions and processes of ionisation and recombination are believed to place the atom or molecule in a peculiar condition, in which it can emit energy to the ether or absorb energy from it. Under ordinary conditions the atom does not seem capable of doing this. In sodium vapour, for instance, according to present theories only one atom in thousands is taking part in absorption at any one time. The problem as to how energy is transferred to and from matter is one of the most fundamental problems of science. A striking example of the fact that a few atoms under peculiar conditions have the power of absorbing an enormous amount of energy from the ether is exhibited by the iron absorption lines in the solar spectrum. An arc of carbon electrodes containing iron as an impurity emits enough iron vapour to absorb as much as the iron vapour in the sun. It is thus seen that an infinitesimal amount of iron in the very great atmosphere of the sun is sufficient to absorb a large part of the energy emitted by the photosphere.

Our present theory of the mechanism of the absorption and emission of radiations is very simple. Light and heat are electro-magnetic radiations, and hence the emitter and the absorber must either be an electric charge or a magnetic pole. As free magnetic poles are unknown to us while free electric charges are known, this theory makes the electric charge the origin of all electro-magnetic phenomena. At present no positive electric charges are known to be associated with portions of matter smaller than the hydrogen atom. On the other hand, negative electrons are known to be associated with masses only about one two-thousandth that of the hydrogen atom. As far as experiment shows, these electrodes always have the same properties and the same charge (the charge is invariably considered as constant when e/m varies), no matter from what element they may come. It is for these reasons that the electron is made the basis of all electro-magnetic theory, and at present there are but few phenomena capable of any explanation which cannot be explained by this theory.

Electro-magnetic radiations then have their origin in electric charges. Continuous spectra (as from hot metals) are due to free electrons, and these apparently have very little connection with the chemical constitution of the metal molecules. Fine line and band spectra are apparently due to different systems of electrons within the atom, and are greatly affected in intensity by the presence of neighbouring atoms. The electrons of this type vibrate in definite frequencies that can be changed only very slightly by changing the external conditions.

The Absorption Spectra of Organic Compounds.

The Unit of this Absorption.— In discussions concerning the colour of organic compounds it is customary to speak of the selective absorption as being due to certain ions or molecules. This is probably true in the infra-red; the electric charges absorbing these long wave-length radiations are probably associated with masses of molecular size. But in the visible and ultra-violet portions of the spectrum the value e/m of the absorbers is invariably of the same magnitude as that of the electron. Drude (*Ann. Phys.*, 1904, xiv., 677, 726, 936, 961) has investigated a large number of organic compounds, and shows that the absorber of all the shorter waves of the spectrum is the negative electron. Houstoun (*Nature*, May 20, 1909; *Proc. Roy. Soc.*, 1909, A, lxxxii., 606) has calculated the value of $e/m = 1{\cdot}297\ V\ K\ \frac{\lambda_1 - \lambda_0}{\lambda_0^3}$ for the absorption bands of several organic compounds, and also shows that the absorber is the electron (V is the refractive index, K the maximum value of the coefficient of extinction; λ_0 is the wave-length of maximum absorption, and λ_1 is the wave-length for which the coefficient of extinction has a value equal to half its maximum. The formula used is based on the present theories of dispersion). The following table is from Houstoun :—

Compound.	λ_0.	e/m.
Fuchsine in alcohol	5500	$1{\cdot}8(10)^7$
Phloxin in water	5150	1·4 „
Crystal violet in alcohol ..	5750	4·9 „
Corallin in alcohol	4650	$1{\cdot}6(10)^8$
Methylen blue in water ..	6650	5·4 „
Water blue in water	5750	8·1 „
Eosin in water	5150	6·9 „
Cyanine in alcohol	5870	5·8 „

Throughout the present paper the absorbers are considered as negative electrons. These electrons have certain free periods corresponding to the bands of selective absorption. These free periods are greatly modified by the presence of certain chemical radicals, and seem to be electrons that are situated either in the outer parts of the atom or between two or more atoms. Stark and others call these the valency electrons, and consider that chemical valency is due to them. Chemical bonds will then be closely associated with the electric fields of these electrons.

While the theory in its present state is confronted with many difficulties, yet it seems a step towards the explanation of the more or less vague chemical bond. As an aid to our imagination, we shall consider atoms or ions as large spherical regions throughout which a positive charge is uniformly distributed. These regions are sometimes spoken of as "spheres of influence." Two atoms collide when their "spheres of influence" touch. Groups of atoms composing ions, radicles, or molecules, will have "spheres of influence. No ion can penetrate the sphere of influence of another atom or molecule. On the other hand, the electrons are very small, and bear much the same relations in size to the atom that the sun bears to the solar system. The electric fields of the electrons occupy quite large volumes, however, although the energy of this field is mostly situated in a very small space. Electrons can therefore move through ions and atoms if they have sufficient velocity. In most organic compounds it is considered that the valency electrons move in the interatomic spaces with considerable ease. In the metals a large number of the electrons are free. In organic compounds that are transparent to certain wave-lengths, the electrons in general will be held within certain regions by forces which are supposed to be elastic in their nature.

(To be continued).

NOTICES OF BOOKS.

An Elementary Course on Food-testing. By B. A. BURRELL, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 1910.

IT must be admitted that the author of this book had a very difficult task before him when he attempted to write a book on food testing which could satisfactorily be used by students who had absolutely no previous knowledge of chemistry, and who presumably wanted to know only as much as would be immediately useful to them. It seems more than probable that the effect produced in the average mind after working through the course outlined in the book would be one of complete bewilderment. The great difficulty in writing such a book is of course that of emptying one's own mind of all knowledge of chemistry and looking at the subject entirely from the point of view of the uninitiated, who has no idea of what details are important and what unimportant. Thus such information—to be found quite at the beginning—as "the contents of the test-tube now consist of a solution of calcium chloride" is quite unnecessary and even deleterious, for the worker is not supposed to know anything about the nature of a chemical reaction. Such points as these show the weakness of the author's method. Moreover, the course is far too ambitious, for quantitative work is introduced; for example, the use of Fehling's solution and microscopic analysis is outlined. The verdict on the book must be that the author has not succeeded in an undertaking in which at best only partial success is possible.

Seeing the Invisible. By JAMES COATES, Ph.D., F.A.S. Second Edition. London: L. N. Fowler and Co. New York: Fowler and Wells Co. 1909.

THE sub-title of this book, "Practical Studies in Psychometry, Thought Transference, Telepathy, and Allied Phenomena," gives some idea of its contents, and it only remains to be said that it is written in a fair spirit which invites unbiassed criticism. The incidents related in it and the arguments put forward are such as to demand the careful attention of thoughtful men, and the author impartially points out some difficulties and discrepancies. The second edition has been somewhat enlarged, and a fresh chapter on "Psychometrical Reflections," based upon the results of personal experimentation, has been added.

CORRESPONDENCE.

EFFLORESCENCE OF WASHING SODA CRYSTALS.

To the Editor of the Chemical News.

SIR,—In reference to a note which appeared in the CHEMICAL NEWS of December 23rd (vol. cii., p. 311) on "Efflorescence of Washing Soda Crystals," I have received the following letter, which gives a very probable explanation of the excess of CO_2 which was noted. With Mr. Howard's approval, I am sending you a copy of his letter. —I am, &c.,

ALEX. C. CUMMING.

Chemistry Department, University of Edinburgh,
January 19th, 1911.

ALEXANDER C. CUMMING, Esq.,
Chemistry Department, University of Edinburgh.

DEAR SIR,—I have noted with much interest your note in the CHEMICAL NEWS on "Efflorescence of Washing Soda Crystals." The presence of the extra half molecule of CO_2 is difficult to explain, as in fifty years' experience I have never found "soda crystals" take up CO_2 from the air. I would venture to suggest a possible origin for the crystals you examined. In old days, when alkali contained much sulphate, it was easy to obtain large perfect crystals of hydrated monocarbonate of soda, but it was most difficult to prevent their falling to pieces under a shade. Therefore for exhibition purposes we used to expose them to an atmosphere of CO_2, and if carefully done the bicarbonate (or sesquicarbonate as the case might be) preserved the form of the original crystal, forming an opaque pseudomorph of perfect shape. If this is the origin of the carbonic acid in these crystals, it in no wise takes away from the interest of the formation of a true sesquicarbonate.—I am, Yours faithfully,

DAVID HOWARD.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Royal Society of Arts, 8. (Cantor Lecture). "Etching," by F. Wedmore.

TUESDAY, 31st.—Royal Institution, 3. "Heredity," by Prof. F. W. Mott, F.R.S., &c.

—— Royal Society of Arts, 4.30. "Tin Resources of the Empire," by F. Douglas Osborne.

WEDNESDAY, Feb. 1st.—Royal Society of Arts, 8. "Examinations and their bearing on National Efficiency," by P. J. Hartog, M.A

—— Society of Public Analysts, 8. (Annual General Meeting). "Detection and Estimation of Small Quantities of Antimony," by P. Schidrowitz and H. A. Goldsbrough. "Analytical and Microscopical Examination of Compound Liquorice Powder," by G. E. Scott-Smith and J. Evans. "Commercial Analysis and Arithmetic," by C. A. Seyler.

THURSDAY, 2nd.—Royal Institution, 3. "Recent Progress in Astronomy," by F. W. Dyson, Astronomer Royal.

—— Chemical, 8.30. "Constancy of Water of Crystallisation of Hydrated Salts," by H. B. Baker and G. H. J. Adlam. "Different Methods of Applying the Grignard Reagent," by H. Davies and F. S. Kipping. "Orientation of the Nitro-group in Nitromyristicinic Acid," by A. H. Salway. "Condensation of Aromatic Aldehydes with Nitromethane," by F. G. P. Remfrey. "The Phosphoric Acids," by A. Holt and J. E. Myers. "Determination of Solubility Coefficients by Aspiration," by W. J. Jones. "The Triazo-group —Part XVI., Interaction of Nitrosates and Sodium Azide," by M. O. Forster and F. M. van Gelderen.

FRIDAY, 3rd.—Royal Institution, 9. "Grouse Disease," by A. E. Shipley, F.R.S.

SATURDAY, 4th.—Royal Institution, 3. "Problems in the Career of the Great Napoleon," by Arthur Hassall, M.A.

THE CHEMICAL NEWS.

Vol. CIII., No. 2671.

THE WORK OF THE CHEMICAL LABORATORIES OF THE BUREAU OF MINES.*

By J. K. CLEMENT.

The chemical work is divided among a number of separate laboratories, each carrying on its own lines of work under the direction of its own chief, the whole forming a group of more or less independent units. The relation of the work of the several chemical laboratories to that of the other departments of the Bureau varies with individual cases. In general, however, the problems of the chemists are closely connected with those of the mining and mechanical engineers.

The Fuel Testing Laboratory is occupied mainly with the analysis and calorimetric testing of fuels, including coal, coke, lignite, and peat. In addition to analysing samples of all fuels used in the boiler and gas producer tests of the Bureau, ultimate analyses and calorific value determinations are made on mine samples of coal collected by the U.S. Geological Survey, as well as by certain State Geological Surveys. The data on these latter tests are of value in establishing the composition and heating value of the coals in connection with the classification of the coal-fields of the United States.

In addition to the laboratory at Pittsburg, there is located in Washington, D.C., a laboratory in which are tested samples of coal delivered to the various buildings, arsenals, navy-yards, and military posts within the district of Columbia, and in various parts of the country, and of the coal purchased by the Panama Railroad,

Fusibility and Clinkering of Coal Ash.

In the use of coal under steam-boilers, the property next in importance to its calorific value is perhaps the fusibility of its ash. Indeed, some coals, which have a high heating value, are worthless for making steam on account of their tendency to clinker and adhere to the grate bars. The relation between the fusibility and clinkering properties of coal-ash and its chemical and mineralogical composition is now being investigated.

It is interesting to note that TiO_2 was found in all the clinkers examined in amounts varying from 1 to 3 per cent. Determinations of the fusion-point of various ashes give values ranging from 1150° to 1400° C.

Chemistry of Petroleum Technology.

The Bureau is making a study of the commercial bodies contained in the crude petroleums of the United States, of the methods for their separation and purification, and of their economic uses. The California fields, because of their showing at this time the greater promise of a large and continued production, their proximity to naval stations, and the peculiar adaptability of their product as a maritime and a locomotive fuel, have been selected for first study. Besides the determination of the properties and uses of the various products of the petroleums of the country, an investigation is being made of the processes of distillation and of the methods of refining.

Combustion Investigations.

The processes of combustion in the boiler-furnaces are being investigated in a furnace specially designed for the purpose. By taking simultaneous samples of the combustion gases, the progress of the reactions may be followed, and the time or space necessary for the complete combustion of various coals, and under varying conditions of operation, may be determined.

The process of producer gas formation is being studied from a physical-chemical standpoint, and an attempt will be made to apply on a commercial scale the results of laboratory experiments an the rate of formation of carbon monoxide and water-gas.

The Composition of Coal.—Our scientific knowledge of the chemical character of coal is limited almost entirely to its chemical analysis and its adaptation to certain industrial operations. The object of one of the investigations of the Bureau is the isolation and identification of some of the constituents of coal. By the use of inert solvents, it has been found possible to extract as much as 35 per cent of the original coal. A number of different substances have been isolated, and the analysis and molecular weights of some of these substances have been determined. In a few cases it is believed that the materials are practically pure substances.

The Volatile Matter of Coal.—The quantity and composition of the gases evolved from various coals when heated to temperatures of from 400° to 1000° C., have been determined. In the experiments which are now in progress, particular attention will be given to the influence of the rate of heating on the character of the gases produced, to the initial composition of the gases at the instant of liberation, and to the thermal decomposition of these gases during passage over heated surfaces.

Weathering and Deterioration of Coal.—In co-operation with the Navy Department, the Panama Railroad Company, and the University of Michigan, the Bureau is conducting an extensive series of tests on the deterioration of various coals in storage, both in the open air and when submerged in fresh water and sea-water.

The Accumulation of Gas from Coal.—The quantity and rate of formation of inflammable gas from freshly mined coal, at ordinary temperatures, and the rate of absorption of oxygen by the coal have been determined.

The Spontaneous Combustion of Coal is being investigated by the Bureau. Statistical information will be combined with the results obtained in the laboratory.

The Burning of Coal in Mines under a Diminished Supply of Oxygen.—The factors governing the propagation or extinguishing of fires in mines are being investigated. Chief among these are variations in temperature and in the oxygen content of the surrounding atmosphere.

Examination of Mine Gases.—Examination is made of samples from normal mine air, from the after-damp following explosions, from stagnant areas, and from burning areas during mine fires. Particular attention has been given to the detection of small amounts of carbon monoxide. By analysing samples during the progress of mine fires, the chemist has assisted in combating fires. The effect of variations of barometric pressure on the exudation of methane and the influence of carbon dioxide on the explosibility of mine gases are being investigated.

The Chemistry of Explosives.

Chemical analyses are made of all explosives submitted to the Bureau for test, of the products of combustion of explosives, and of electric detonators, blasting-caps, and fuses. All explosives, blasting-caps, electric detonators, and fuses purchased by the Isthmian Canal Commission are inspected by representatives of the Bureau, and all shipments of such explosives are sampled and analysed.

Coal-dust Explosions.—The two greatest sources of danger encountered in mining operations are the explosive gases given off by the coal, and the finely divided coal-dust which exists throughout most coal-mines. The first danger can be overcome by increasing the ventilation in the mines. Unfortunately, this increases the danger from the coal-dust by the removal of its moisture.

A laboratory method has been devised to test the inflammable character of samples of coal-dust, and to classify them according to their inflammability. This method is based on determining the amount of combustion which

* Abstract of a Paper read before the Minneapolis meeting of the American Chemical Society.

takes place when clouds of dust of the same density are ignited under the same conditions; the amount of combustion being determined by the pressure developed within the explosion vessel. In this way it is possible to obtain results on any one sample of coal-dust which agree to 3 to 5 per cent of the total pressure developed.

One af the proposed means of lessening the inflammable character of coal-dust is to add a non-inflammable dust. The laboratory method used to investigate the inflammability of coal-dust has been extended to various percentages of coal-dust and finely-ground shale in order to determine to what extent the combustion is limited by the presence of the inert dust. The experiments indicate tbat a marked diminution of pressure is not obtained until about 25 per cent of inert dust is added, the pressure then falling off rapidly with a further increase in the amount of shale-dust added.

SEPARATION OF OXYGEN BY COLD.*

By JAMES SWINBURNE, F.R.S.

(Concluded from p. 42).

So far I have discussed the subject on what are sometimes incorrectly called theoretical lines, that is to say ideal lines, in which all sorts of assumptions are made so that the discussion should be easier. Thus I have discussed perfect heat insulation, and completely reversible changes and perfect thermodynamfc engines. The principles are the same on a large scale; but there is leakage of heat, and all sorts of irreversible changes of heat, and a compression pump does not come up to the thermodynamic ideal in efficiency. In the industry as now carried on the question of efficiency is of very little importance. Oxygen is sold in small quantities in bottles, and the costs of compressing, handling, selling, delivering, and so on, and the collection of the empties, are enormously large in proportion to the mere cost of making. Thus we have discussed oxygen taking 34,000 joules for 230 grms., or about 2 k.-w. hours per cubic foot.

The great future for the separation of the gas is in the direction of making nitrogen for the manufacture of calcium cyanamide, and oxygen for use in blast-furnaces, and other work where a high temperature may be worth the extra cost. It is therefore important to see how far the gases can be produced on a large scale at prices within a reasonable margin.

We may therefore sum up the rectifying part of the plant as an apparatus which gives up heat at a low temperature, say, 82° A, and absorbs heat at, say, 90° A, the heat taken in at 90° A being equal to that given out at 82° A. A refrigerator must therefore be a thermodynamic engine capable of giving heat at 90° A, absorbing heat at 82° A, and giving out heat at the temperature of the works, say, 290° A.

It is generally supposed that Linde depended on an irreversible expansion of a gas. This is not the case, and I would put the matter in another way.

If gas is compressed, cooled to, say, 290° A, and sent into an interchanger, out of which it comes by a return pipe at the pressure of the air, there must be cooling going on inside, as the air delivered has higher internal energy than the air going in. You have therefore an apparatus for producing cold—that is to say, for absorbing heat at a temperature below the room. The question is, What is the lowest temperatu.e at which this apparatus will take in heat? The lowest temperature is that of the boiling-point of the liquefied gas at the pressure of the atmosphere. If the apparatus is working in such a way that it can take in heat H at temperature θ_2 the increase of entropy is H/θ_2. But if instead of work ng in this way the heat is taken in at θ_1, which is a higher temperature, the increase of entropy is H/θ_1, which is less, so the apparatus makes up the deficit of entropy by irreversible expansion. On starting up a Linde machine it begins by abstracting heat from its own air and metal-work at the temperature of the air, so the entropy is made up by irreversible expansion. As the temperature at which the heat is absorbed falls the irreversible expansion gets less and less, until finally the whole of the gas is turned into liquid. Then there is some production of heat by the liquid passing from a high to a low pressure through an obstruction, and also some slight evolution of gas to cool the released liquid from the boiling-point under the high to the boiling-point under the low pressure. The irreversible loss due to liquid is $pv/10$ in joules, where v is the volume of the liquid. If the compression is small this is small, but if it is high pv may be considerable. It would be quite easy to get this energy out by means of a little engine, as there is no expansion and no difficulty in lubrication, and it would be worth while on a large scale. The liquid may also be cooled to a lower boiling-point while still under pressure, so that there is no irreversible evolution of gas on its being exhausted from the engine.

The refrigerator has to do the work of two thermodynamic engines, for it has to abstract a lot of heat at one temperature, give a large proportion back at a higher temperature, and give out heat at the temperature of the works. The ideal apparatus consists of a compressor with water-cooling delivering gas at the temperature of the works and a high pressure to an interchanger. The pressure is chosen so that the gas liquefies under it at 90° A, giving up its heat to the rectifier. The liquid at 90° A is then cooled in an interchanger to 82°, and it is then passed through a hydraulic engine, coming out at atmospheric pressure and temperature 82°. It is now vaporised, taking in heat at 82°, and goes out by the delivery side of the interchanger.

This process described is not quite reversible, because the specific heat under constant pressure of the gas coming down the interchanger is greater than that of the gas coming up under atmospheric pressure; there has therefore to be an abstraction of heat all along the interchanger to make up for this difference.

The idea of this apparatus is something like that of an ordinary carbonic acid machine worked under different conditions. If a carbonic acid machine were worked in the tropics and the cooling water were above the critical-point of CO_2, the compressor would supply compressed gas only. Some sort of refrigerator would be necessary to liquefy the CO_2, and the liquid CO_2 would then be evaporated at a low temperature. We thus have three temperatures to consider—the temperature of the works at which heat due to compression is given out, the temperature at which the CO_2 is liquefied under pressure, and the temperature at which the CO_2 is finally evaporated. In a refrigerating plant three temperatures would be a nuisance, so a fluid is chosen with a critical-point above the temperature of the works. But for rectifying three temperatures are necessary—the temperature of the works, the temperature of the boiling-point of the least volatile liquid, and the temperature of the liquefaction of the mixture. We can therefore use a fluid which is compressed at a temperature which may be much above its critical-point.

Fig. 4 shows an ideal Linde refrigerator. The compressor A delivers a fluid, say, air under pressure, to the cooler B. Heat comes out there at the temperature of the works. The air goes on down through the interchanger C until it is cooled to 90° A. Then it is cooled in D, which is really a coil of pipe immersed in the oxygen to be evaporated at the bottom of the rectifier. From D the liquid, still under pressure, goes down the interchanger until it is cooled to 82° A, and it then works a little engine E, and comes out into F. F is really a coil of pipe in the liquefier of the rectifier. The air is evaporated in F, and passes up the interchanger, and escapes at G.

There are some points to be noticed. As already pointed out the interchanger must take in heat by leakage, which

* A Paper read before the Faraday Society, December 13, 1910.

is an irreversible process; and the heat taken in at F will be greater than that given out at D, as it takes more heat to vaporise a liquid at a low pressure and temperature.

The processes in this refrigator are, however, substantially reversible.

If schemes for dealing with liquefied gases are examined, it will often be found that a liquid is being condensed or evaporated by a gas in the interchanger. That is always a piece of bad design, involving irreversible change. It may be inevitable, of course; but it is an evil which must be carefully watched.

(Note.—There is another fallacy very common with regard to gas issuing from a nozzle. Suppose it comes out into the atmosphere, it is thought that as it has to expand against the pressure of the atmosphere, doing work in joules equal to a tenth of its increase of volume, it must be cooled to a corresponding degree. This is a mistake nearly everyone makes until he thinks of the matter a second time. As such an error would give rise to many miscalculations in connection with the liquefaction of gas, it is not impertinent to call attention to it).

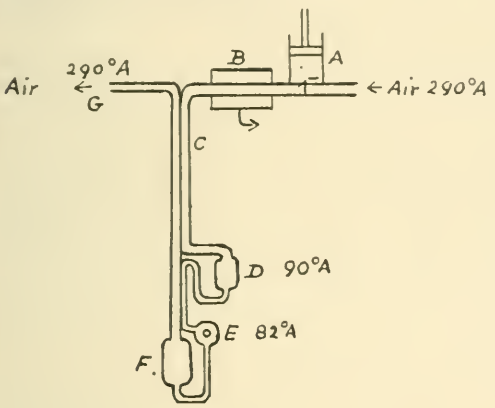


Fig 4.

Linde points out that the mechanical work necessary may be reduced by working between two high pressures. But there is a limit to this, as if both pressures are very high the lower temperature limit of the plant is reduced; so the limit is reached by the lower pressure, which must be low enough for the fluid to evaporate at 82° A, or whatever temperature the heat has to be extracted from the rectifier. If we choose a fluid—say, nitrogen—this gives the lowest pressure that can be used. Then the other pressure must be high enough for the liquid to condense at 90° A. Some latitude can be got by control of the pressures in the rectifying plant, but it is simpler for the present to take the rectifier as working at atmospheric pressure for the sake of ease of calculation. The refrigerator, then, has to supply for each kilo of air split into pure gases 135,000 joules at 90° A, absorbing 135,000 at 82° A. The liquefying of this fluid is in contact with a fluid that is being evaporated, so that that part of the process is ideally reversible. The re-evaporation is in contact with the air which is being liquefied, so that part of the process is ideally reversible. The passage of the liquid from the high to the low pressure can very easily be made to give out work. It is not the same problem as dealing with expanding air, as the volume is small, the pressure constant, and the liquid acts as a lubricant. The process, so far, is essentially reversible. The specific heat of compressed gas is higher than that of the same gas at a lower pressure, so a little allowance must be made for that. It is thus possible to use a process which has no external work done by expansion of cooled gas in such a way as to get little loss by irreversible changes.

To work out an example, nitrogen can be taken as the fluid, as it is easier to discuss than a mixture. To get 135,000 joules, taking heat of vaporisation of nitrogen 200 joules per grm., we need 675 grms. of nitrogen, and we can liquefy this at 90° A under about four atmospheres, evaporating it again at 82° A at two atmospheres. Taking the density of liquid nitrogen as 0·8 the hydraulic engine gives out 170 joules, a mere trifle in this case, and the compression of the nitrogen from two to four atmospheres needs 37,000 joules, so we need under 37,000 joules. As the separation needs 40,000 this is clearly an erroneous figure, but the data are very uncertain. We must need more than 40,000.

To work on a large scale with atmospheric pressure in the separator and four and two in the refrigerator would be quite out of the question. The volumes of air would be enormous, and the interchanges would be very inefficient. Those who have had to work with gases that have to be heated or cooled will realise the extent of this trouble at once. To make the plant practical it will be necessary to work the rectifier under pressure. This raises the temperature of the rectifier; but that does not mean that we can separate the gases more economically; the cost of separation depends, as already stated, on the difference of entropy of the gases entering and leaving the plant, not on what goes on in the plant, provided there are no irreversible changes. Using pressure allows the refrigator to be worked at higher pressures, so that the interchanger may become practical.

Assuming the ideal energy needed to separate a kilo of air into its gases to be 40,000, the question is, What will it cost in practice? On a large scale it may be safe to say 100,000 joules. We would thus get 230 grms. for 100,000 joules; or a ton would need 120,000 k.w. hours. Taking the cost of a killowatt hour as low as 0·1d., this means £50 a ton.

It does not look as if oxygen at this order of figure could be used for blast-furnace work. Taking a blast-furnace as using four and a-half tons of air per ton of iron, to increase the oxygen content by 1 per cent of the oxygen content comes out at 10s. per ton of pig. This does not look as if it could be of use.

The principle of separating gases by cold can be applied to other gases. Thus hydrogen may be purified, so that water-gas can be used as source of balloon gas. Methane can be separated out by solution in water under under pressure. Chlorine can be separated from the impure gas from the anode chambers in electrolytic works. Such chambers are generally worked under a slight exhaust to avoid troubles due to leaks. Air thus leaks in, and the chlorine coming off is moist and impure. Chlorine can be condensed into water, and it might appear that condensing such gases as chlorine and methane into water would allow of their being separated with less expenditure of energy than the entropy consideration demands. This is not so. It takes greater pressure to get the gas into the liquid out of a mixture than the solution exerts in an atmosphere of the pure gas.

Chlorine, by the way, is easier to handle than is generally supposed. It can be pumped in iron pumps flooded with sulphuric acid. It can also be dried and then compressed in iron pumps lubricated with sperm-oil saturated with chlorine. It is not necessary to dehydrate it absolutely for compression up to, say, 50 lbs.

There may be other gases that can be separated or purified by liquefaction and rectification; it is difficult to think of any case where the principle cannot be applied.

Crystallised Chlorophyll.—M. Tswett.—The green crystals which Borodin separated by means of alcohol from many species of plants, and to which the name "crystallised chlorophyll" has recently been given, can be shown by adsorption analysis to be an isomorphous mixture of two chlorophylline derivatives, α- and β-metachlorophylline. These agree spectroscopically with their mother-pigments, and obviously contain their unaltered chromophores.—*Berichte*, xliii., No. 16.

AN ORGANO-METALLIC BODY OF THE ANILINE SERIES.

(PRELIMINARY NOTE).

By E. RATTENBURY HODGES.

THE fact that aniline acts, in some cases, as an altered ammonia is of interest, and it has already been pointed out that it precipitates neutral salts of zinc, and also alumina as hydrates.

To about 60 cc. of a saturated aqueous solution of aniline, a solution of zinc chloride of the usual reagent strength was added drop by drop.

At first there were no signs of a reaction, but within a few minutes a slight murkiness appeared, and a little later an abundant crop of fine colourless and highly refractive crystals developed.

Beneath a low power these appear to belong to the quadratic system.

A rough qualitative examination showed that the crystals constitute a well defined double salt of zinc and aniline chloride.

This salt slowly dissolves in cold, but more readily in slightly warmed water. With a clear bleaching powder solution it gives the characteristic purple reaction.

A mixture of aniline with anhydrous zinc chloride yielded quite different results.

January 19th, 1911.

DETERMINATION OF FILLERS IN RUBBER MIXTURES.*

THE present methods for the determination of filler in rubber, viz., boiling with petroleum or with xylol under pressure, are of little use if the rubber contains any easily decomposed sulphides as antimony sulphide in red rubber or carbonates which easily give off CO_2 as $MgCO_3$. For such cases it seems necessary to look for a solvent which will dissolve the rubber at temperatures below the decomposing temperatures of the fillers.

The D.R.P. 202850 pertains to a process for the regeneration of old rubber by treatment with high boiling ethers of the aliphatic, aromatic, and of the heterocyclic series at 100° to 130° and the subsequent precipitation of the rubber by means of alcohol.

It seemed possible that this process could also be used in the analysis of rubber goods.

A series of trials has shown that by extended heating with anisol or phenetol (fatty aromatic) ethers at 90° to 120° good vulcanised para rubber can easily be brought into solution. The antimony sulphide remaining behind remains unchanged (its decomposition point is 130—140°) and also retains its red colour. The magnesium carbonate is also unaltered. The determination is carried out as follows:—

The finely divided rubber is leached with acetone to remove all free sulphur. 1 grm. of the extracted rubber is warmed to 90—120° with 30 cc. of anisol or phenetol in a weighed Erlenmeyer flask of about 200 cc. capacity till the rubber is all dissolved and the antimony sulphide and other fillers are on the bottom of the flask. For this from one to two hours is necessary, depending on the rubber itself.

After solution the flask is nearly filled with benzene and the mixture centrifuged. The clear liquid is poured off, the residue washed a few more times with benzene, and finally centrifuged with alcohol and ether. It is then dried at 105° and weighed. Some of the results will soon be published in "Die Mitteilungen aus dem Kgl. Material prufungaamt."

* Translated from the *Chemiker Zeitung* for the *Chemical Engineer*, xii., No. 5.

ON AN INDIRECT METHOD FOR DETERMINING COLUMBIUM AND TANTALUM.

By H. W. FOOTE and R. W. LANGLEY.

Introduction.

THE determination of tantalum and columbium in mixtures of their oxides has always been one of the difficult operations in analytical chemistry. The method for separating the two metals was devised by Marignac (*Archiv. des Sci. Phys. et Nat.*, 1866), and consisted in separating by crystallisation the difficultly soluble potassium-tantalum fluoride from the more soluble columbium salt. This method, with various minor modifications, is still the one commonly used. The operations involved are tedious, and the results are only approximate. Judging by our own experience, the method requires some practice before even approximate results can be obtained. The reason why the results are inaccurate is, first, because the tantalum salt obtained is not quantitatively insoluble, so that tantalum is left in the filtrate with the columbium; and second, because of the tendency of columbium to crystallise to a limited extent with the tantalum double fluoride.

Two volumetric methods have been proposed, both depending on a preliminary reduction of columbium to a lower oxide and titration with potassium permanganate. By the first of these methods (Osborne, *Am. Journ. Sci.*, 1885, [3], xxx., 329) columbium is reduced by zinc in strong hydrochloric acid solution, and titrated with potassium permanganate which has been standardised by means of a pure columbium salt. In the second method (Metzger and Taylor, *Zeit. Anorg. Chem.*, 1909, lxii., 383), columbium in a solution containing succinic acid is reduced by amalgamated zinc. Under fixed conditions, by this method, columbic oxide is reduced to the empirical oxide, $Cb_{20}O_{31}$, and can be titrated with permanganate.

The method of separation proposed by Weiss and Landecker (*Zeit. Anorg. Chem.*, 1909, lxiv., 65) will be discussed in a later article.

The low density of columbic oxide (4·552) as compared with the density of tantalic oxide (8·716) suggested that the composition of any mixture of the two could be deduced from its density, if the density of mixtures of known composition was first determined. The principle has been applied by Penfield and Ford (*Am. Journ. Sci.*, 1906, [4], xxii., 61) to the estimation of the proportions of tantalic and columbic oxides in stibiotantalite, assuming that the density of mixtures of the oxides is a linear function of the composition. The problem consisted in preparing various known mixtures of the two oxides under definite conditions and determining the densities of the mixtures.

Methods and Errors.

We first investigated the method to be used to determine the density. The mixed oxides as they are obtained in analysis are very fine powders. After some preliminary work the following method for determining density was adopted. The ordinary form of bottle pycnometer of 10 cc. capacity was used. The stopper was carefully ground to fit, using fine carborundum powder. The capacity was re-determined from time to time, but it remained nearly constant. The unweighed material was finely powdered and placed in a small beaker half full of water. The water was boiled hard for a half-hour by passing in an electric current through a fine spiral of platinum wire suspended in the water, the powder being stirred up a number of times during the operation. The water could not be boiled in a beaker over a flame on account of severe bumping, as the powder settles rapidly. The boiling can be accomplished over a flame, however, if a rough platinum dish is substituted for the beaker and the liquid stirred continually. The contents of the beaker were cooled, most of the water poured off, and the residue washed through a funnel into the pycnometer with boiled water. Any powder on the neck of the pycnometer was washed

down and the pycnometer filled to overflowing. Any powder or air-bubbles floating on the top were swept off with a glass rod. Air-bubbles did not usually adhere to the sides, but were always looked for and removed with a wire if present. The pycnometer was placed in a tank of water and kept at 20° C. for twenty minutes. The stopper was then inserted, the top quickly wiped off, and the whole dried and weighed at once. The contents were transferred to a platinum dish, evaporated to dryness, and ignited finally over a blast for five minutes. In transferring the contents of the pycnometer to the dish it was found that all loss could be avoided if the pycnometer were inverted over the dish and shaken slightly till the powder left the bottom. By then bringing the mouth against the side of the dish the mixture will run out quietly. Two or three rinsings with water are necessary. The pycnometer usually contained a trace of oxide sticking to the sides, which might weigh as much as 2 mgrms. It was therefore dried at 120° C. and weighed to determine the small amount of oxide. This method gave results which were entirely satisfactory for our purpose. The average difference between duplicates in forty determinations of density amounted to 0·22 per cent. This result includes several determinations in which the amount of material used was under 1 grm., which increased the percentage error considerably. When 2 grms. or more of material were used, duplicates seldom disagreed by more than 0·15 per cent. To illustrate: the densities found for a mixture containing 90 per cent tantalic oxide were 8·103 and 8·078 when 1·5 grm. were used. Upon repeating the experiment with 3·3 grms. of material, the densities found were 8·090 and 8·092.

We next determined that the mixed oxides became constant in density after heating for an hour over the blast-lamp. For this purpose a sample of the mixed oxides from a Branchville columbite was ignited over the blast-lamp for an hour in a platinum crucible. The density was determined, and the material then ignited for five-minute periods, a density determination being made after each ignition. The results were: 4·908, 4·908, 4·919, 4·921, 4·923, 4·912. The material was then heated an hour longer, and the density re-determined, the results being 4·924 and 4·923. In these and the following determinations the ignition was accomplished in 30 grm. platinum crucibles over a fairly powerful blast-lamp. The question whether different preparations of the oxides in the same proportions had the same specific gravity could only be answered by making a series of such determinations. Complete duplicate series of mixtures were not made on account of lack of material, but the results given in the accompanying table show what agreement was obtained in each case. The average difference in density between different preparations of oxides having the same composition was 1·1 per cent. This appears to be the greatest source of error in the determinations, and shows that the method of preparing the oxides must be fixed as definitely as possible.

The detailed method of preparing the mixed oxides in condition for specific gravity determination was as follows: —About 3 grms. of the oxides were fused in a platinum dish with six times their weight of acid potassium fluoride till the mass was just liquid. The fusion was dissolved in 200 cc. of hot water in a platinum dish, adding a little hydrofluoric acid to obtain a clear solution. The solution was made alkaline with ammonia, and after allowing the precipitate to settle, filtered on a rubber funnel and washed well with water containing ammonia. The precipitate runs through the paper if pure water is used. The precipitate was re-dissolved in the platinum dish, using as little dilute hydrofluoric acid and water as possible, and evaporated to dryness. Ten cc. of concentrated sulphuric acid were added in such a way that the residue was completely moistened. The liquid was evaporated over asbestos till all hydrofluoric acid was expelled, stirring if there seemed to be danger of spattering. The residue was cooled, 200 cc. of water added, and the solution made alkaline with ammonia, filtered, and the precipitate washed with dilute ammonia. The precipitate was transferred while moist to a 30-grm. platinum crucible and ignited over a blast-lamp for an hour. The residue was ground to a fine powder with water and was then ready for the density determination previously described. This method of preparing the oxides may appear longer than necessary, but we adopted it only after preliminary work had made it appear essential. Acid potassium fluoride was used in decomposing the oxides instead of potassium bisulphate, because the latter does not render the oxides completely soluble in hydrofluoric acid if they have previously been ignited. This fusion with acid fluoride does not involve any loss of either columbium or tantalum by volatilisation. To prove this, 1·3576 grms. of mixed columbic and tantalic oxides were subjected to the process outlined above, and 1·3603 grms. were obtained. If the mixed oxides have not been ignited and are completely soluble in hydrofluoric acid, this may be used to dissolve them instead of acid potassium fluoride. The first precipitate with ammonia from hydrofluoric acid solution cannot be ignited and used for density determination, as it contains fluorine after being ignited. Washing the precipitate with dilute ammonia will not remove all the fluorides.

Results.

In preparing the mixtures for density determinations, we were fortunate in obtaining very pure tantalum and columbium oxides. Dr. W. E. Ford supplied a sample of columbic oxide which had been given him by Prof. E. F. Smith. It had been prepared from the chloride, and was exceedingly pure. Dr. Ford also supplied some tantalum oxide from Dr. W. R. Whitney, of Schenectady, who stated that the material was considerably over 99 per cent pure. Dr. T. B. Osborne furnished us with considerable amounts of potassium tantalum and potassium columbium double fluorides, which we re-crystallised and converted into the oxides. The densities were as follows:—

Columbic oxide	(Smith)	4·552
,,	,, (Osborne)	4·564
Tantalic	,, (Whitney)	8·716
,,	,, (Osborne)	8·683

In making the mixtures, it was assumed that Smith's and Whitney's oxides were pure and that Osborne's columbic oxide contained 0·61 per cent tantalic oxide and his tantalic oxide 0·32 per cent columbic oxide. These values were calculated from the densities. The original intention was to make mixtures of the oxides at intervals of 10 per cent. Irregularity in the curve showing change in density with change in composition when there was over 60 per cent of tantalic oxide caused us to repeat some of the determinations in this region, as we suspected an error in the work. We were led to the conclusion that in the mixtures containing a moderate excess (65—85 per cent) of tantalic oxide, the densities are not as constant as when other proportions are present. The table and curve given below will make this clearer. All the results which were obtained upon known mixtures are tabulated below with one exception. This result was obviously in error, as the density was not approximately related to the composition. In most cases, the density of one mixture of any given composition was determined. Where the curve as plotted from the table showed irregularities, duplicate mixtures were made and the results enclosed in brackets in the table. All densities are referred to water at 20°.

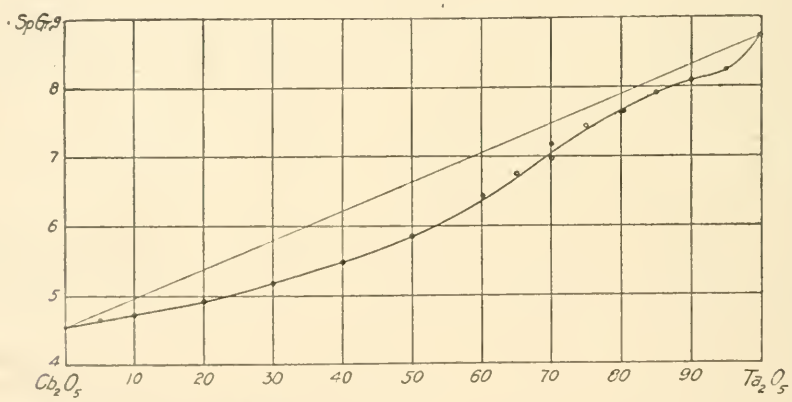
The average of the results in the table are plotted in the figure.

The curve has some interest from the standpoint of solid solutions. The fact that the points as plotted do not lie on a straight line indicates that the oxides have formed a solid solution and not a mechanical mixture. The irregularities in the curve, which can hardly be due entirely to experimental error, suggest that the oxides are not soluble in each other in all proportions, but that tan-

talum oxide has taken up about 18 per cent of its weight of columbium oxide, and the latter over twice its weight of tantalum oxide. The intermediate mixtures would then consist of mechanical mixtures of each oxide saturated with the other. In these mixtures the variations in densities of different mixtures of the same composition are greatest. Points on this part of the curve should lie on a straight line if the interpretation of these results as suggested is correct.

Composition. Per cent Ta_2O_5.	Specific gravity.				Average. specific gravity.
0	4·555	4·549			4·552
5	4·632	4·647			4·650
10	4·744	4·748			4·746
20	4·929	4·929			4·929
30	5·203	5·197			5·200
40	5·474	5·474			5·474
50	5·852	5·847			5·850
60	6·437	6·431			6·434
65	6·719	6·763	6·730		6·737
(70	7·189	7·170			7·083
(70	6·958	6·992	7·008	6·981)	
75	7 431	7·452			7·441
(80	7·629	7·637)			7·654
(80	7·662	7 687)			
(85	7·885	7·925	7·963)		7·961
85	8·01	7·99			
(90	8·103	8·078	8 133)		8·098
(90	8·090	8·092			
95	8·245	8·241			8·243
100	8 725	8·684	8·730		8·716

FIG. 1.



Analyses of Minerals by Density Method.

The analysis of a sample of stibiotantalite from the Brush collection was carried out using the indirect method for determining the relative proportion of tantalum and columbium oxides. The density of the sample was 6·80 and the weight 4 grms. The method used was as follows:—Two 1 grm. samples and a 2 grm. sample were each dissolved in about 20 cc. of hydrofluoric acid. Some white insoluble material remaining undissolved was filtered off, and its weight deducted from that of the sample taken. The resulting weight was taken as that of stibiotantalite used for analysis. The solution containing an excess of hydrofluoric acid was diluted to 300 cc. and hydrogen sulphide passed in until all antimony and bismuth were precipitated as sulphides. The precipitate was filtered, washed with water, and treated several times with yellow ammonium sulphide. The insoluble residue of bismuth sulphide was dissolved in nitric acid, precipitated with ammonium carbonate, filtered, washed, ignited, and weighed as Bi_2O_3. The solution of antimony sulphide in ammonium sulphide was precipitated with sulphuric acid (in the case of the 2 grm. sample one-tenth of the solution was used), filtered in a porcelain Gooch crucible, and washed with water. The crucible was supported in a triangle on a sand-bath, and covered with a 300 cc. flask whose bottom had been removed. A glass tube and thermometer were fitted into the neck of the flask through a rubber stopper. The air in the flask was displaced by a rapid stream of carbon dioxide entering through the neck of the flask and escaping through the sand at the bottom. The temperature was raised to 240° and maintained for two hours, while carbon dioxide was passed in. At the end of this time all free sulphur had been removed from the Sb_2S_3 precipitate, as was shown by the weight remaining constant after further treatment. The crucible was allowed to cool in the atmosphere of carbon dioxide, its weight taken, and Sb_2S_3 calculated into terms of Sb_2O_3.

The filtrate from the precipitation with hydrogen sulphide contained columbium and tantalum in solution in hydrofluoric acid. It was evaporated to dryness, moistened with concentrated sulphuric acid, and heated until all hydrofluoric acid was expelled. Water was added, and the solution made alkaline with ammonia, filtered, the precipitate washed, ignited, and weighed. After heating over a blast-lamp for an hour the density was determined. In experiments 2 and 3 the hydrofluoric acid solutions containing tantalum and columbium were united in order to obtain enough material for a reliable determination of density. The results of the analysis are given below.

The density method was also applied to the partial analysis of a Branchville columbite, and for comparison tantalum and columbium were separated and determined by the Marignac method. The specimen contained no titanium. The oxides obtained in the course of analysis were soluble in hydrofluoric acid, so that preliminary fusion with acid fluoride was unnecessary. The solution was precipitated with ammonia, filtered, re-dissolved in hydrofluoric acid, and evaporated with sulphuric acid, &c., as previously described. The results of the duplicate analysis are given in the following table:—

	1.	2.	3.	Average.
Sb_2O_3	40·98	40·98	40·91	40·95
Bi_2O_3	—	0·50	0·69	0·60
Ta_2O_5	41·53	42·30	42·30	41·92
Cb_2O_5	16·56	15·82	15·82	16·19
		99·60	99·72	99·66
Density of mixed oxides Ta and Cb	7·191	7·282	7·282	7·236

$$\text{Ratio of } \frac{Sb_2O_3 + Bi_2O_3}{Ta_2O_5 + Cb_2O_5} = 0{\cdot}92$$

	1.	2.
Per cent $Ta_2O_5+Cb_2O_5$ in mineral	78·77	79·04
Density of mixed oxides	4·957	4·918
Per cent Ta_2O_5 in oxides by density method	21·0	20·0
Per cent Ta_2O_5 in oxides by Marignac method	18·74	17·21
Per cent oxides in mineral by density method .. .. { Ta_2O_5 ..	16·54	15·81
	Cb_2O_5 ..	62·23	63·23
Per cent oxides in mineral by Marignac method .. .. { Ta_2O_5 ..	14·43	13·60
	Cb_2O_5 ..	63·68	65·75

It will be seen that the results are approximately alike by the two methods, but we believe the results by the density method are more accurate and they are certainly much easier to obtain. The specific gravity of the columbic oxide from one Marignac separation was found to be 4·612, corresponding to 96 per cent of columbic oxide and 4 per cent tantalic oxide, showing that some tantalum went with the columbium. It is probable also that some columbium crystallised with the tantalum double fluoride, but the amount of tantalic oxide was too small for a density determination.

The authors wish to express their thanks to Dr. W. E. Ford and Dr. T. B. Osborne for the tantalum and columbium oxides used in this investigation.—*American Journal of Science*, xxx., No. 180.

REPORT ON CHEMICAL CONSTITUTION AND THE ABSORPTION OF LIGHT.*

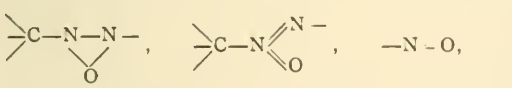
By W. W. STRONG.

(Continued from p. 48).

The Theory of Chromophores.

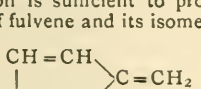
In considering absorption spectra it is often quite sufficient to speak qualitatively of the colour of different compounds. The introduction of certain groups into colourless compounds often results in a coloured compound. Any such group is a chromophore. Sometimes the chromophore may be weak, and it may require the addition of several chromophores to produce a coloured compound. Ultimately the colour is due to absorbers existing in the chromophore—probably the valency electrons. Among the better known chromophores are the groups :—

$>C=C<$, $=CO$, $>C=NH$, $-CH=N-$, $-N=N-$,

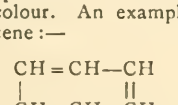


$=N=O$, $=C=S$, $-C-S_2-C-$.

The ethylene group $>C=C<$, is a weak chromophore, and several chromophores must be present before the absorption is sufficient to produce colour. An example is that of fulvene and its isomer, benzene :—



Fulvene.



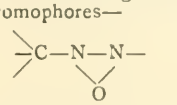
Benzene.

Benzene is colourless and exhibits absorption only in the ultra-violet, whereas fulvene is an orange-yellow.

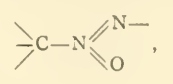
The carbonyl group, $=C=O$, is also weak, and several of the groups must be present in a compound to produce colour. The following examples indicate how an increasing number of the carbonyl groups produces a greater and greater absorption of the shorter wave-lengths :—

R—CO—R	Colourless
CH_3—CO—CO—CH_3	Yellow
C_6H_5—CO—CO—C_6H_5	Yellow
CH_3—CO—CO—CO—CH_3	Orange
C_6H_5—CO—CO—CO—CO—C_6H_5..	Red

The combination of two phenyl groups causes absorption only in the ultra-violet. The introduction of the $-CH=N-$ chromophore is sufficient to produce colour, as is shown in the yellow benzylideneaniline, $C_6H_5CH=N-C_6H_5$. The azo-chromophore, $-N=N-$, produces the same effect, as shown in the orange azobenzene, $C_6H_5-N=N-C_6H_5$. The chromophores—

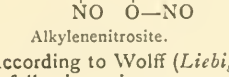


and

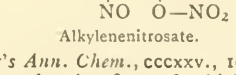


on the other hand, are very weak.

The nitroso group, $-N=O$, is a very strong chromophore when it is joined to a carbon atom directly. The effect of this chromophore is shown in nitrosobenzene, $ON-C_6H_5$, which is of a green colour. Wallach (*Liebig's Ann. Chem.*, ccxli., 288; cccxxii., 305), and recently J. Schmidt (*Ber.*, xxxv., 2323, 3721; xxxvi., 1768), have investigated the following compounds, which are of a deep blue colour :—

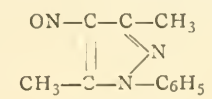


Alkylenenitrosite.

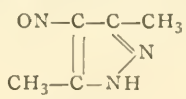


Alkylenenitrosate.

According to Wolff (*Liebig's Ann. Chem.*, cccxxv., 192), the following nitroso compounds, the first of which is green and the second blue, have the structures :—

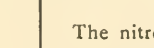


1-Phenyl-3.5-dimethyl-4-nitrosopyrazol.



3.5-Dimethyl-4-nitrosopyrazol.

The carrier of the colour in these cases is the $C-N=O$ group. Many of the aliphatic nitroso compounds show polymerisation and are then often colourless. The polymerisation of $R-N=O$ to $(RNO)_2$ is probably accompanied by a rearrangement as follows :—



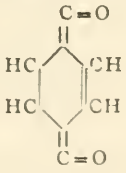
This would explain why the polymer is colourless.

The nitro-group, or , is a very weak chromophore. The aliphatic nitro-compounds, CH_3NO_2, $C_2H_5NO_2$, &c., are colourless. When combined with other chromophores, coloured compounds, such as nitrobenzene or nitronaphthalene, can be obtained. Stobbe (*Ber.*, 1905, xxxviii., 4082) has investigated the influence of the nitro-group on the fulgides. In solution the *p*-nitrophenyl-fulgide has a deep red colour. The ortho and meta compounds are much less deeply coloured.

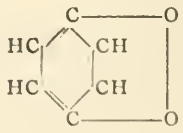
Hantzsch (*Ber.*, xxviii., 2744) and Raschig (Dammer's "Handb. der Anorg. Chemie") have shown that the $=N=O$ group acts as a chromophore in the sulphonate, $O=N=(SO_3K)_2$, which is violet in solution and orange in the solid state. The thiocarbonyl group, $=C=S$, is a rather strong chromophore. Examples are the blue compounds, thioacetophenone, $C_6H_5-CS-CH_3$, and thiobenzophenone, $C_6H_5-CS-C_6H_5$. For a fuller account of the colour properties of various compounds, the reader is referred to Ley's paper (*Jahrb. d. Rad. u. Elek.*, 1909, vi., 274), from which the data here recorded have been largely taken.

* This Report is based upon an article by H. Ley, entitled "Ueber die Beziehung Zwischen Lichtabsorption und Chemischer Konstitution bei Organischen Verbindungen." See *Jahrbuch der Radioaktivität und Elektronik*, 1910, vi., 274. From the *American Chemical Journal*, xliv., No. 1.

There has been a great deal of discussion whether quinone has the folmula I. or II.

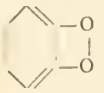


I.



II.

Willstätter and F. Müller (*Ber.*, 1908, xli., 2580) have found that *o*-benzoquinone can exist in two forms, I. and II., the former being colourless and the latter red :—



I.

II.

This fact may possibly explain several outstanding difficulties among quinone derivatives. It would be expected that the substitution of an (NR) group for oxygen in a quinone would give a deeply coloured substance. As a matter of fact, quinonediphenylimide—

$$C_6H_4N=\langle\rangle=NC_6H_5,$$

is brownish red. But the compounds $NH:C_6H_4:NH$ and $O:C_6H_4:NH$ are colourless. This can easily be explained if the latter compounds are assumed to have the superoxide formula similar to that of *o*-benzoquinone. The quinone chromophore enters into the composition of quite a large number of coloured compounds.

The space relations of the chromophores seem to affect the colour of compounds. For instance, the ethylene group can have two isomeric configurations :—

$$\begin{array}{l} R-C-H \\ \quad\| \\ R'-C-H \end{array} \quad \text{or} \quad \begin{array}{l} R-C-H \\ \quad\| \\ H-C-R' \end{array}.$$

This geometric isomerism may explain the following facts :—

1. Diethoxynaphthostilbenes (Elbs, *Journ. Prakt. Chem.*, xlvii., 72), $C_2H_5O-C_{10}H_6.CH:CH.C_{10}H_6.OC_2H_5$. The form which has the highest melting-point is colourless, while the lower melting form is yellow.

2. Dibenzoylethylenes, $C_6H_5CO.CH:CH.COC_6H_5$ (Paal and Schulze, *Ber.*, xxxiii., 8795; xxxv., 168). The higher melting form is colourless, while the lower melting form possesses a deep yellow colour.

That the colour-producing power of the chromophores is due to the double bonds seems quite certain. When these bonds are saturated the resulting compounds are colourless.

Coloured.

$C_6H_5-N=N-C_6H_5$	Azobenzene
$C_6H_5-N=O$	Nitrosobenzene
$O=C_6H_4=O$	Quinone
$C_6H_5.CO.CO.CO.C_6H_5$ ..	Diphenyltriketone

Colourless.

$C_6H_5NH-NHC_6H_5$	Hydrazobenzene
$C_6H_5-N.H.OH$	Phenylhydroxylamine
$HO.C_6H_4.OH$	Hydroquinone
$C_6H_5.CO.CH_2.CO.C_6H_5$ ..	Dibenzoylmethane

The different di- and tri-substitution products usually give rise to different absorption bands when the absorption is selective. Ortho- and metaxylene have one band, whereas paraxylene has two. The following gives the value of the limit of absorption when light is passed through a grm. molecule of the substance ;—

	Cresol.	Dihydroxybenzene.	Hydroxybenzoic acid.
Meta	3433	3466	3359
Ortho	3413	3399	3080
Para	3359	3151	2986

When a chromophore is introduced into a compound the bands may be shifted towards the red or towards the violet. The former effect is bathochromous, the latter hypsochromous. The effect of joining chromophores is usually bathochromous. For example :—

	λ.	λ.	λ.	λ.
Benzene	2610	2540	2450	2440
Naphthalene	2850	2720	2630	2550
Anthracene	—	3600	3430	3280

In triphenylmethane the limit of the visible portion of the spectrum is reached. It may be stated here that anthracene and phenanthene have entirely different absorption spectra, although the fluorescent spectra are very similar (Elston, *Astrophysical Journ.*, 1907, xxv., 3). An auxochrome is a radical that causes the absorption to be more intense. An example is $-CO-C=C-CO-$, which appears in the indigos—

$$C_6H_4\langle^{CO}_{NH}\rangle C=C\langle^{CO}_{NH}\rangle C_6H_4,$$

and also in the deeply coloured compounds.

$$C_6H_4\langle^{CO}_{O}\rangle C=C\langle^{CO}_{O}\rangle C_6H_4,$$

$$C_6H_4\langle^{CO}_{S}\rangle C=C\langle^{CO}_{S}\rangle C_6H_4.$$

The groups CH_3, OCH_3, C_2H_5, the halogens, &c., are bathochromes, while the groups NO_2 and NH_2 are hypsochromes.

The infra-red absorption spectra to about 15 μ of a large number of organic compounds have been investigated by W. W. Coblentz ("Investigations of Infra-red Spectra," Carnegie Publication No. 35). Isomeric compounds are found to possess very different absorption, depending on the bonding of the atoms in the molecule. Stereomeric compounds, on the other hand, were found to possess the same absorption spectra. The replacing of hydrogen by an NH_2 or CH_3 group usually results in the appearance of new bands. In the spectrum of certain benzene derivatives, however, the benzene spectrum is usually present. The carbohydrates investigated had characteristic spectra with absorption bands at 0·83 to 0·86 μ; 1·67 to 1·72 μ; 3·25 to 3·43 μ; 6 75 to 6·86 μ; and 13·6 to 14 μ. The three isomeric xylenes have banded spectra in which the most important line in each group lies farthest toward the long wave-lengths in the order ortho, meta, and para.

The author (*Phys. Rev.*, Dec., 1909; Feb., 1910) has shown that the effect of the NO_3 group and of free nitric acid is hypsochromous, causing the uranyl bands to shift towards the violet. The effect of free hydrochloric acid or of zinc, aluminium, or calcium chlorides on the uranyl chloride bands is bathochromous. Recently the author has found that the NO_3 group is hypsochromous with respect to the neodymium and erbium bands.

(To be continued).

Royal Institution.—On Thursday next, February 9, at 3 o'clock, Dr. P. Chalmers Mitchell begins a Course of three lectures at the Royal Institution on "Problems of Animals in Captivity"; and on Saturday, February 11, Dr. Thomas G. Jackson, R.A., delivers the first of three lectures on "Architecture—the Byzantine and Romanesque Period." The Friday Evening Discourse on February 10 will be delivered by Sir Sidney Colvin, on "Robert Louis Stevenson"; on February 17, by Prof. Henry E. Armstrong, on "The Stimulation of Digestive Activity"; and on February 24, by Prof. Jean Perrin, on "Mouvement Brownien et Realité Moleculaire" (in French).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 19th, 1911.

Sir Alexander Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Action of* B. lactis aerogenes *on Glucose and Mannitol.*" (Part II.). By G. S. Walpole.

The "crude glycol" obtained by the action of *B. lactis aerogenes* on glucose contains two optically inactive 2:3 butane diols, whose diphenylurethanes melt at 199·5° and 157° respectively. The former constitutes well over 90 per cent of the material. If fructose be substituted for glucose in one of the flasks, the yield of "crude butylene glycol" and acetylmethyl carbinol is of the same order as when glucose is employed. Acetylmethyl carbinol is formed abundantly when the bacillus is cultivated in a solution of butylene glycol in 1 per cent peptone in a current of oxygen.

"*Pharmacological Action of* Gonioma Kamassi (*South African Boxwood*)." By Dr. W. E. Dixon.

South African boxwood, *Gonioma Kamassi*, has been employed occasionally in Lancashire as a substitute for common boxwood in the manufacture of shuttles; it is stated that symptoms of poisoning have occurred in a small proportion of the men engaged in sawing this wood or finishing the chiselled shuttles.

From the wood an alkaloid can be obtained to about 0·07 per cent. This has a very characteristic physiological action which places it in the curare group of drugs. The members of this group may be regarded as possessing three actions in common. (1) Paralysis of certain nerve cells; (2) increase of spinal and medullary reflexes; (3) paralysis of motor nerve endings.

Boxwood exerts all these effects. It paralyses the nerve cells in the brain and medulla as well as those on the course of the vagus and sympathetic nerves, and therefore after its exhibition to animals the stimulant action of nicotine cannot be obtained. In small doses the reflexes are increased, and if an injection be made into a vein going to the spinal cord of an animal, strychnine-like convulsions are produced. Boxwood causes death by paralysing the respiration; this is central in origin, but it occurs at a time when the phrenics and intercostals are depressed though not paralysed. Boxwood has no direct action on the heart or on other form of muscle.

Reasons are given for believing that the recorded cases of poisoning are not due to the specific action of the drug after absorption, but to the effect of the drug in facilitating certain local reflexes principally of a respiratory nature in the predisposed.

"*Autoagglutination of Red Blood Cells in Trypanosomiasis.*" By Dr. W. Yorke.

Autoagglutinin exists in small quantity in the blood of many normal animals. It is frequently present in much greater quantity in the blood of animals infected with trypanosomes.

Reaction between autoagglutinin and erythrocytes takes place only at low temperatures. The strongest reactions are obtained when a suspension of washed erythrocytes in normal saline solution is treated at 0° C. with plasma, which has been prepared by defibrinating blood at 37° C.

Autoagglutinin can be removed from plasma by absorption with the erythrocytes of the same animal. The reaction between autoagglutinin and red blood cells is reversible, the clumps disappearing on warming and reappearing on cooling.

Iso- and hetero-agglutinin are also often present in much greater amount in the blood of infected animals than in that of normal animals of the same species.

From the red blood cells of an infected animal, which have been agglutinated in the cold by the plasma of the same animal, an active substance can be extracted with normal saline solution at 37° C. This substance agglutinates not only the red cells of the same animal and other members of the same species, but also those of many animals of different species. Observations of this kind indicate that auto-, iso-, and hereto-agglutinin are not different highly specific substances, but have closely related affinities.

That a clumping together of the red blood cells is frequently observable in coverslip preparations of the fresh blood of animals and man infected with trypanosomiasis, is due to the existence of an excess of autoagglutinin in the plasma, which reacts with the erythrocytes to a certain extent at the temperature (15—20° C.) at which the preparations are usually made.

It is to be inferred from the information at present available that a marked degree of autoagglutination of red blood cells is an extremely rare occurrence apart from an infection with trypanosomes. The phenomenon is therefore of some value as a diagnostic sign.

"*Transformation of Proteids into Fats during the Ripening of Cheese.*" (Preliminary Communication). By M. Nierenstein.

Contrary to the accepted view, it was found that the so-called ripening of cheese is not accompanied by a transformation of proteids into fats. The increase of weight of the latter, as observed by other workers, being due to the presence of *free cholesterol, aminovaleric acid, putrescine and cadaverine* in the ethereal extract. This investigation disproves one of the frequently quoted evidences in favour of the theory that proteids serve as a source for the fat-formation in the animal body.

"*Action of X-rays on the Developing Chick.*" By J. F. Gaskell, M.A., M.B.

No difference was observed in the action of X-rays upon any one tissue rather than another.

The action is confined to the lowering of the mitotic activity of the growing tissues.

If this diminution is not too great, complete recovery occurs, and the chicks hatch out at the usual time. If the diminution is above a certain degree, recovery does not take place, and further development is arrested forthwith.

The critical dose, which just prevents recovery, varies with the stage of development of the embryo, decreasing as the mitotic index decreases.

The "mitotic index" as defined by Minot represents the number of mitoses per 1000 cells in the various tissues of embryos of various ages; and he has shown that throughout embryonic life a rapid diminution of mitotic activity is going on. He calls the figures obtained the mitotic index for that particular tissue.

"*Experiments to Ascertain if Antelope may act as a Reservoir of the Virus of Sleeping Sickness* (Trypanosoma gambiense). By Colonel Sir David Bruce, C.B., F.R.S., A.M.S.; and Captains A. E. Hamerton, D.S.O., and H. R. Bateman, R.A.M.C. (Sleeping Sickness Commission of the Royal Society, Uganda, 1908—10).

It is known that the tsetse flies (*Glossina palpalis*) around the northern shores of the Victoria Nyanza still retain their infectivity for sleeping sickness, in spite of the fact that the native population was removed from the Lake-shore some three years ago.

A series of experiments was, therefore, carried out to ascertain if the antelope, which are fairly common along the uninhabited shores of the Lake, were capable of acting as hosts of the parasite of sleeping sickness.

Eleven antelope of the waterbuck, bushbuck, and reedbuck species were obtained from a district where tsetse flies and sleeping sickness did not exist. Blood from these animals was first inoculated into monkeys to ascertain if

they were already naturally infected with trypanosome disease. They proved to be healthy in this respect. Tsetse flies (*Glossina palpalis*) that were known to be infected with the virus of sleeping sickness were then fed upon each of the eleven antelope. After about eight days the blood of these animals was again inoculated into susceptible animals, with the result that the latter became infected with *Trypanosoma gambiense* in every case.

In eight out of the eleven buck under experiment *Trypanosoma gambiense* appeared in their blood for a few days only (some seven to twelve days) after they had been bitten by infected flies.

Flies that were hatched out in the laboratory, and had never fed before, were now fed upon the infected antelope, and subsequently upon monkeys. After an interval of about thirty days, required for the development of trypanosomes within the fly, monkeys were infected with sleeping sickness from the antelope by the agency of *Glossina palpalis* in sixteen out of twenty-four experiments.

On dissecting the flies which had been fed upon the infected antelope it was found that 10·8 per cent of them were infected with *Trypanosoma gambiense*. The highest percentage of infected flies in any one of the positive experiments was 21 per cent; the lowest was 1·3 per cent.

Nine of these antelope infected with *Trypanosoma gambiense* were under daily observation for over four months. They remained in perfect health.

Two of them (a waterbuck and a bushbuck) never showed trypanosomes in their blood although examined every day. Both these antelope-infected flies fed upon them, one of them as long as fifty-five days after its infection.

No wild antelope inhabiting the Lake-shore has yet been found to be naturally infected with *Trypanosoma gambiense*.

"*Experiments to Ascertain if the Domestic Fowl of Uganda may act as a Reservoir of the Virus of Sleeping Sickness* (Trypanosoma gambiense)." By Colonel Sir David Bruce, C.B., F.R.S., A.M.S.; and Captains A. E. Hamerton, D.S.O., and H. R. Bateman, R.A.M.C. (Sleeping Sickness Commission of the Royal Society, Uganda, 1908—10).

There is evidence that tsetse flies (*Glossina palpalis*) feed on the blood of birds as well as that of mammals inhabiting the shores of Victoria Nyanza.

Domestic fowls, as representing birds, were experimented with in the search for possible hosts or reservoirs of the virus of sleeping sickness. A series of twenty-one experiments was carried out to ascertain:—

1. If these birds can, like antelope, be infected with *Trypanosoma gambiense* by the bites of known infected flies.
2. If birds so infected can transmit the parasite to newly-hatched *Glossina palpalis* which had not fed before they were allowed to bite the fowls.
3. If these flies can convey sleeping sickness to normal monkeys.

About 2000 flies, many of which had been proved to be infected with virulent *Trypanosoma gambiense*, were fed upon twenty-one domestic fowls. The results were negative in every case, as ascertained by frequent microscopical examination of peripheral and centrifuged heart's blood, and inoculations of the fowls' blood into susceptible animals.

Four hundred newly-hatched flies were fed upon three of the fowls which had been bitten by infected flies. The former were subsequently fed upon monkeys, with the result that they failed to convey sleeping sickness from fowls to monkeys.

Two hundred and eighty-three of these flies were dissected, and no flagellates could be found in them.

Conclusion.—The Uganda fowl cannot act as a reservoir of the virus of sleeping sickness.

NOTICES OF BOOKS.

The Encyclopædia Britannica: A Dictionary of Arts, Sciences, Literature, and General Information. Eleventh Edition. Cambridge: At the University Press. 1910.

We have received for review the Eleventh Edition of the Encyclopædia Britannica. In this first notice we propose to give a preliminary survey of the work as a whole, and to point out a few instances in which it differs from its predecessor the Tenth Edition. Turning over the pages and comparing articles on similar subjects, it is obvious that an enormous advantage has been gained by the simultaneous preparation and publication of the whole Encyclopædia as one complete work. This is the first time such a brilliant feat has been attempted, and, indeed, without a system of perfect organisation, direction, and supervision equal to the generalship in an active military campaign, backed by inexhaustible funds, such a task would have been impossible. "The man behind the gun" is the one to whom success is due; to the Editor-in-Chief, Mr. Hugh Chisholm, we owe the successful accomplishment of this gigantic undertaking.

For all practical purposes the whole field of human knowledge is concentrated into 29 volumes. A century ago it would not have been difficult to find a man with a considerable if not profound command of all the sciences. To-day such a feat is impossible; but if the saying is true that next to knowing a thing one's self the next best thing is to know where to put one's hand on the information, the owner of this Encyclopædia for practical purposes may consider himself the master of all knowledge. The rest is only a matter of intelligent reading and memory.

The excellent scientific essays in the last edition—where attempt was made to combine under one heading all, or nearly all, the subjects belonging to the science under discussion – have now been abandoned in favour of the more useful arrangement of sub-branches of the science under the alphabetical headings where the student would be most likely to look for them.

To give a general illustration of the treatment of scientific subjects in the Eleventh Edition and how it differs from the plan followed in the Tenth Edition, we will take the subject "Chemistry."

Under this heading, in the Eleventh Edition, the science is discussed as a whole, its history and general aspects in relation to other subjects are examined; but the details of the separate branches falling within the subject matter of Chemistry are given in separate articles, to which cross-references in the general article "Chemistry" act as pointers. For instance, in the old edition the subject "Alkali Manufacture" had no separate heading, and the student had to read through 120 pages of the article "Chemistry." But the present edition contains a special article on "Alkali Manufacture" running into 11 pages, fully illustrated with drawings of the most recent machinery and furnaces.

"Chemistry" commences with a section on the "History of Chemistry"; followed by one on the "Principles," providing an introduction to the terminology of Chemistry. Then come sections on "Inorganic Chemistry," "Organic Chemistry," "Analytical Chemistry," and "Physical Chemistry." The general subject of "Chemical Action" is written by W. Nernst, whilst "Chemistry" is from the pen of C. Everett. Under each subject are numerous cross-references, among which we may pick out such different departments of the Science as Alchemy, Calorimetry, Capillarity, Crystallography, Electrolysis, Electro-metallurgy, Energetics, Fluorescence, Isomerism, Photochemistry, Refraction, Radio-activity, Spectroscopy, Stereoisomerism, Thermo-chemistry, Thermodynamics, and Valency.

Among subjects more closely connected with the practice of Chemistry references are given to articles on Adulteration, Acid, Atom, Condensation of Gases, Distillation, Element, Indicators, Molecule, Medicine, Solution, and Weighing Machines; whilst among chemical bodies

we find references to Acidamines, Alizarine, Alloys, Argon, Arsenic, Azo and diazo-compounds, Dyeing, Helium, Hydrazine, Indigo, Oximines, Phosphorus, Polymethylines, Purin, Quinones, Sugars, and Terpenes. Besides the above subjects and others to which references are given in the main article on Chemistry there are shorter articles not specially pointed out scattered throughout the twenty-eight volumes, giving a description of nearly every chemical compound likely to be looked for. To show the completeness of the editing we have gone through the first volume, which includes words between "A" and "AND," and have picked out the following headings under which the body named receive full treatment. They are :—

Abraum salts, Accumulator, Acenaphthene, Acetic acid, Aceto-acetic ester, Acetone, Acetophenone, Acetylene, Acid, Acidamines, Acmite, Aconite, Acridine, Actinometer, Adenine, Adulteration, Aërated waters, Aether, Affinity, Agate, Air, Albertite, Albite, Albumin, Alchemy, Alcohol, Aldehydes, Alembic, Alexandrite, Alizarin, Alkali, Alkali manufacture, Alkaline earths, Alkaloid, Allophane, Allotropy, Alloxan, Alloxantin, Alloys, Allyl alcohol, Almandine, Alum, Aluminium, Alunite, Amalgam, Amazon stone, Amber, Ambergris, Amianthus, Amidines, Amines, Ammonia, Amorphism, Amperometer, Amphibole, Amygdalin, Amyl alcohols, Amyl nitrite, Anaesthesia, Analcite, Analysis, Analyst, Anatase, Anatto, Andalusite.

This comprehensive plan is followed out in other sciences, and it has the great advantage that in a science like Chemistry, in which the branches are so numerous and involved, each sub-subject can be relegated to a specialist in that particular branch ; for Chemistry to-day is so bewildering, so vast and complicated that no one man, however eminent, can hope to become an authority in more than a few departments. By the sectional plan here adopted the articles which together make up the science of chemistry give a better and truer up to date survey than could have been obtained had a complete article been written by one man. Any objection which might be taken against the "dictionary" arrangement of subjects in preference to the complete collection under one heading, is removed by the number of cross references. This has been rendered possible by the fact that the whole work has been prepared simultaneously, so that every branch of chemistry, from Acid and Atom to Yeast and Zinc, could be laid out in proof on the table for the general Science Editor's collocation into a consistent whole by the addition of the necessary references.

In the spelling of chemical names we are glad to see the usual mode adopted, and the English reader is spared the shock of suddenly meeting such words as buret, chlorid, and sulfur. It is also an advantage to retain the spelling of "gramme" instead of "gram." In hurried writing chemists, like others, are not always careful to dot "i's," and we have known serious mistakes between grains and grams owing to this omission.

A great drawback to the last edition of this Encyclopædia was its ponderous weight and bulk. To-day the employment of very light and opaque India paper has diminished the weight of each volume from over 8 lbs. to under 3 lbs. Reference to any subject is now easy ; a delicate lady can refer to any volume without effort, whilst to look up a subject in the former edition was a task for an athlete.

Change is the Law of Life as well as of Encyclodædias, but for the present we may put our faith in this new edition of an unsurpassed work of reference.

Laboratory Notes on Organic Chemistry. By Paul Haas, D.Sc., Ph.D. London: Macmillan and Co., Ltd. 1910.

The practical work in organic chemistry given in the syllabus of the medical examinations of London University is well treated in this book. It opens with descriptions of methods of determining physical constants, with special reference to biochemistry. Methods of calculating results are carefully explained, and typical examples are worked out. The second section describes some important preparations, the substances chosen for discussion being judiciously selected and well grouped, while general principles are always emphasised. Quantitative and qualitative analysis are next treated, and finally the reactions of some important organic substances are given in detail. It will be observed that the order in which the subjects are taken is rather unusual, but since each section is quite independent of the preceding and complete in itself it would be easy to make alterations if it were considered desirable. The experimental directions for the performance of quantitative analysis are in some cases somewhat curtailed, and occasionally they appear to need some slight revision. For instance, in the description of the determination of fat by Soxhlet's method it is doubtful whether seven or eight syphonings would be invariably sufficient to extract the whole of the fat. On the other hand, the section on the reactions of organic substances is particularly good, formulæ and equations being very abundant. In an appendix some theoretical matters are discussed ; for example, the law of mass action, which is very well treated, and a brief outline is given of the chemistry of colloids.

The Organic Chemistry of Nitrogen. By Nevil Vincent Sidgwick, M.A. (Oxon.), Sc.D. (Tübingen). Oxford: The Clarendon Press. 1910.

This book is based upon a series of advanced lectures on organic chemistry given at Oxford, and as they were intended for students and their aim was mainly educational, excess of detail is avoided, and general principles and historical development are emphasised. The organic compounds containing nitrogen are well classified in four groups, considered in the order in which they are most profitably studied. Thus the first section deals with the esters of nitrous and nitric acid, *i.e.*, those compounds in which no nitrogen atom is directly attached to carbon. Part II. includes the numerous and important compounds in which one nitrogen atom is attached to carbon, and in Part III. open chains of two or more nitrogen atoms are treated. The last section discusses the most important typical compounds of the closed ring class. The whole treatment is excellently systematic and clear, and the portions dealing with the application of the methods of physical chemistry in the study of organic compounds are particularly stimulating and interesting. Careful examination shows that the book is thoroughly well got up and well printed, the only misprint which could be found being among the equations on page 25.

Institute of Chemistry.—Pass List, January Examinations, 1911.—Of nine candidates who presented themselves for the Intermediate Examination, six passed —J. Crawford, J. C. Earl, H. J. Evans, W. R. Pratt, D. C. Scott, and G. E. Slim. Of twenty-six candidates who presented themselves for the Final Examination, eighteen passed. In the Branch of Mineral Chemistry—W. C. Davis, W. H. H. Norris, B.A. (Cantab.), B.Sc. (Lond.), and R. W. Pope ; in the Branch of Physical Chemistry—W. R. G. Atkins, B.A. (Dub.), and Bucchok Shen, B.Sc. (Birm.) ; in the Branch of Organic Chemistry—W. Caw, J. C. Duff, B.Sc. (Manc.), A. Greeves, A.R.C.S. (Lond.), B.Sc. (Lond.), W. H. Nodder, B.Sc. (Lond.), T. A. Smith, and T. A. Wallace, B.A. (Dub.) ; in the Branch of the Chemistry of Food and Drugs and of Water—W. H. Dickinson, M.B.Ch.B. (Edin.), Capt. I.M.S., H. D. Ekington, R. H. Ellis, A. D. Heywood, and E. H. Shepherd, B.Sc. (Lond.) ; in the Branch of Biological Chemistry —J. Crabtree, B.Sc. (Manc.). Capt. Dickinson was examined for the Fellowship. One Fellow, R. W. Clarke, also obtained the Certificate in the Chemistry of Food and Drugs and of Water.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other ise expressed.

Zeitschrift für Anorganische Chemie.
Vol. lxix., No. 1, 1911.

Alloys of Tellurium with Cadmium and Tin.—Matsusuke Kobayashi.—From the study of the melting-point curves of mixtures of tellurium and cadmium of different compositions, it appears that a compound TeCd is formed, but it can exist in the melt only in equilibrium with excess of tellurium. With tin a similar compound, TeSn, is formed. These two compounds do not form mixed crystals with their components. Cadmium dissolves up to 1·2 per cent of tellurium at 700°. At higher temperatures the solubility probably increases, but it is impossible to determine it owing to the volatility of the metals.

Rusting of Iron.—V. Andström.—When distilled water is very carefully freed from all dissolved gases by boiling, it can be shown qualitatively that it attacks iron, but the action is so slight that it might be ascribed to traces of oxygen introduced during the experiment. Tap-water submitted to the same preliminary treatment has not a greater effect than distilled water. Tap water containing the usual amount of oxygen and carbon dioxide has a decided action. If carbon dioxide is added to ordinary tap-water, the percentage of oxygen being lowered, it is found that the amount of corrosion is quite independent of the altered amount of CO_2, but bears a definite relation to the dissolved oxygen. The reaction, $Fe+2H_2CO_3=Fe(HCO_3)_2+H_2$, proceeds only very slowly.

Physico-chemical Aspect of the Formation of Cuprous Iodide.—P. P. Fedotieff.—The author has determined the limits of the existence of copper iodide in aqueous solution, and has investigated the influence of the temperature. As the percentage of iodine in the solution increases the solubility of CuI also increases, and similarly as the amount of copper is raised. The author has also determined the equilibrium constant of the formation of copper iodide and the equilibrium constants of the reaction $I'+I_2 \rightleftarrows I_3'$.

Electrical and Mechanical Properties of Alloys of Noble Metals.—Wilhelm Geibel.—The author gives details of the determination of the tenacity of wires of palladium-gold alloys of different composition, from which it appears that this property increases as the percentage of gold increases, reaching a maximum at 55·8 per cent of gold, and then decreasing. The thermo-electric force towards platinum was also determined, and it was found that this decreases as the percentage of gold increases, reaching a minimum at 45 per cent, and then increasing.

Isomorphism of Potassium and Sodium Compounds.—Ernst Sommerfeldt.—The examination of the isomorphism of the two double sulphates, astrakanite and leonite, is difficult owing to the formation of turbid crystals, and investigation under the microscopic shows that astrakanite becomes turbid if it contains more than 0·8 per cent of K_2SO_4. The presence of small particles can easily be recognised in these crystals, and within a short period of time (three days) the number of particles increases by as much as 50 per cent.

Chemistry of Meteorites.—W. A. Wahl.—Meteorite minerals and meteoric rocks are characterised by a smaller percentage of oxygen than is present in the corresponding minerals and rocks obtained from the earth's crust. The crystalline structure of chondrites may be explained by supposing that heating (thermic metamorphism) has occurred, thus obliterating the original tuff structure. The breccia-structure is due to very rapid local heating.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Chemistry of the Lead Chamber Process," by Dr. F. Raschig. (This meeting will be held in the large Theatre King's College).
—— Royal Society of Arts, 8. (Cantor Lecture). "Brewing and Modern Science," by Prof. A. J. Brown.
TUESDAY, 7th.—Royal Institution, 3. "Heredity," by Prof. F. W. Mott, F.R.S., &c.
WEDNESDAY, 8th.—Royal Society of Arts, 8. "Some Nigerian Head-hunters," by Capt. A. J. N. Tremearne, B.A.
THURSDAY, 9th.—Royal Institution, 3. "Problems of Animals in Captivity," by P. Chalmers Mitchell, F.R.S., &c.
—— Royal Society. "Certain Physical and Physiological Properties of Stovaine and its Homologues" and "Effect of Some Local Anæsthetics on Nerve," by Dr. V. H. Veley and W. L. Symes. "Experimental Researches on Vegetable Assimilation and Respiration—VIII., New Method for Estimating the Gaseous Exchanges of Submerged Plants; IX., Assimilation in Submerged Water-plants and its Relation to the Concentration of Carbon Dioxide and other Factors," by Dr. F. F. Blackman and A. M. Smith.
—— Royal Society of Arts, 4.30. "Indian Supersitions," by R. Leslie Moore.
FRIDAY, 10th.—Royal Institution, 9. "Robert Louis Stevenson," by Sir Sidney Colvin, M A., D.Litt.
SATURDAY, 11th.—Royal Institution, 3. "Architecture—the Byzantine and Romanesque Period," by T. G. Jackson.

INDIAN INSTITUTE OF SCIENCE, BANGALORE, INDIA.

CHAIR OF ORGANIC CHEMISTRY.

The Council of the Institute will shortly proceed to elect from amongst the Candidates recommended by an Advisory Committee, a PROFESSOR of ORGANIC CHEMISTRY, who will be expected to take up his duties at the beginning of July, 1911. The salary attached to the Post will commence at £1000 per annum, and will increase by annual increments of £50 to £1250; in addition to this, a sum equivalent to 10 per cent of the salary will be set aside to accumulate at 4 per cent interest to form a retiring allowance. The Professor will be provided with a house in the Institute grounds.

The Institute is mainly conducted for Post-graduate Research, and the duties of the Professor will be such as usually attach to similar appointments in Europe.

The Advisory Committee, which will meet in London, invite applications for the above appointment. Applications, accompanied by five copies of testimonials, must be in the hands of the undersigned (from whom further information can be obtained), by FEBRUARY 28th.

R. WHYTLAW-GRAY,
Secretary to the Advisory Committee.

University College,
Gower Street, London.

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THE CHEMICAL NEWS.

Vol. CIII., No. 2672.

THE ESTIMATION OF IODINE IN ORGANIC COMPOUNDS AND ITS SEPARATION FROM OTHER HALOGENS.*

By A. F. SEEKER and W. E. MATHEWSON.
Assistant Chemists, New York Food and Drug Inspection Laboratory.

In the examination of a number of samples of commercial erythrosin the determination of iodine was considered to be one of the most important factors in establishing the identity and purity of the dye. As many of the colours contained varying amounts of common salt, and contamination with chlorine and bromine substitution products of fluorescein was also to be sought and detected, the problem of estimating iodine under these conditions by a method that would not require a prohibitive amount of manipulation and time presented itself. At first an attempt was made to estimate the total halogens by the Carius method, from which the halogen due to common salt (estimated in another portion after separation of the colour acid) was deducted. A qualitative test for chlorine and bromine in the residue left after ignition of the colour acid with alkali was relied upon to detect these halogens in organic combination.

The Carius method was found to yield erratic and unreliable results with erythrosin, confirming the experience of other analysts with iodine compounds. Linnemann (*Ann. Chem. Pharm.*, 1871, clx., 205) ascribed the difficulty to the solubility of silver iodide in nitric acid containing an excess of silver nitrate. The authors have observed crystals of free iodine in the bomb tubes after removal from the furnace, and on heating they were seen to volatilise with the formation of the characteristic violet vapours. An ample excess of silver nitrate over that required for the iodine present had been added in every case. As the results of the determinations by the Carius method were almost invariably too low, it is the opinion of the authors that some of this free iodine is lost in transferring the oxidising mixture from the bomb tubes.

A number of methods have been suggested for the estimation of iodine in the presence of other halogens in inorganic soluble compounds. Those involving the conversion of iodide into iodate by potassium permanganate (Hempel, *Ann. Chem. Pharm.*, 1858, cvii., 100) have been described by Reinige (*Zeit. Anal. Chem.*, 1870, ix., 39), and by Baubigny and Rivals (*Comptes Rendus*, 1903, cxxxvii., 927). The application of these and of most other methods requires a preliminary destruction of the organic matter, and this, if accomplished in the usual way by fusion with potassium carbonate or a similar alkaline substance, requires much care, and in the case of mixtures containing sulphonated dyes, yields a melt which contains reducing sulphur compounds. These compounds must be removed before the application of Reinige's method, which is also subject to the limitations of volumetric processes in general. With Baubigny's method the distillation requires close attention, and much difficulty was experienced in driving off all chlorine without loss of iodine.

Experiments proved that if a solution containing erythrosin is treated with potassium permanganate and nitric acid the organic matter is completely decomposed, and chlorine and bromine are converted into volatile products, while all of the iodine remains as iodic acid. The permanganate is converted into a voluminous hydrated oxide of manganese. The chlorine apparently is partly liberated as such, and partly converted into an oxygenated compound which is boiled off with difficulty, but may be volatilised in a current of steam, or driven off by evaporating the mixture to dryness on a steam bath. When much chlorine is present the last of it can be removed only by treating the residue twice with nitric acid, and again evaporating to dryness. That no iodine is lost in this process is shown in Table I. Iodine may be determined in the residue left after oxidation by the permanganate by taking up in a little water, adding nitric acid, and then dissolving the oxide of manganese in an excess of sulphur dioxide solution, the iodic acid being at the same time reduced. Silver nitrate is added to the clear solution, which is then boiled until the excess of sulphur dioxide is driven off, and the silver iodide has coagulated. This is filtered, washed, dried, and weighed in the usual manner.

The experimental results given in Table I. were obtained on mixtures containing measured amounts of a solution of pure iodine. To prepare this, re-sublimed iodine was dissolved in a concentrated solution of potassium iodide, and a large part of it then precipitated by the addition of water. The precipitated portion was collected on a perforated plate, thoroughly washed with water, and sublimed. The sublimate was dried over calcium chloride. Portions of this iodine were dissolved in a little alkali, and diluted to definite volume with water, the solutions so prepared being carefully kept in tightly stoppered flasks, and used for the experiments in Table I. The pipettes and flasks used had been standardised at the United States Bureau of Standards.

Table I.—*Estimation of Iodine in the presence of Chlorine and Bromine.*

Chlorine or bromine added. Grm.	Iodine found. Grm.	Iodine recovered. Per cent.	
Series A.—20 cc. of Solution = 0·2640 grm. of Iodine used.			
None	0·2643	100·1	(a)
"	0·2644	100·2	
"	0·2646	100·2	
"	0·2645	100·2	
0·3 sodium chloride	0·2637	99 85	(b)
0·3 potassium bromide	0·2642	100 1	
0·05 sodium chloride + 0·10 potassium bromide	0·2636	99 84	
0·10 sodium chloride + 0·05 potassium bromide	0·2635	99 82	
Series B.—20 cc. of Solution = 0·4885 grm. of Iodine used.			
None	0·4876	99·84	(a)
"	0·4877	99·86	
0·2 sodium chloride + 0·1 potassium bromide	0·4871	99·75	(b)
	0·4885	100·1	

(*a*) Direct precipitation method.
(*b*) Permanganate oxidation method.

In order to test the applicability of the method to the estimation of iodine in erythrosin a sample of this colour was synthesised, the fluorescein, prepared from Kahlbaum's resorcin and phthalic anhydride, being completely freed from chlorides by repeated precipitation from alkaline solution by acetic acid. This was combined with some of the purified iodine just described, and finally separated as the colour acid. This preparation contained no halogen other than iodine, of which the alkaline fusion method indicated 56·40 per cent, as shown in Table II. After further experimental work on the proper proportion of reagents to be employed the following procedure was adopted:—

Place from 0·3 to 0·4 grm. of the erythrosin in a porcelain casserole, dissolve this in 5 cc. of a 10 per cent sodium hydroxide solution, then add 35 cc. of a 7 per cent solution of potassium permanganate. After mixing, cover the vessel with a watch-crystal, and add 10 cc. of nitric acid, keeping the dish covered. Agitate the mixture, place on a steam-bath, and keep covered until spattering ceases, after which remove the watch-glass, and allow evaporation to proceed to dryness. (In the operation of drying

* *Circular* No. 65 United States Department of Agriculture, Bureau of Chemistry.

particular care should be observed to prevent access of reducing gases to the mixture). Treat the residue with 5 cc. of 7 per cent potassium permanganate and 5 cc. of concentrated nitric acid, and again evaporate to dryness. Then add about 50 cc. of water and 5 cc. of concentrated nitric acid to the residue, following this by 40 cc. of a saturated solution of sulphur dioxide, and allow the whole to stand with occasional stirring (breaking up the lumps with a glass rod) until the hydrated oxide of manganese has dissolved. Add an excess of silver nitrate to the clear solution, and boil until sulphur dioxide has been expelled and the silver iodide has flocculated. Filter this, and weigh in the usual manner. The results obtained are given in Table II.

TABLE II.—*Estimation of Iodine in Erythrosin Colour Acid.* (*a*)

Theory, 60·75 per cent.

Amount of colour acid used. Grm.	Other substance added. Grm.	Iodine found. Per cent.	
0·4929	None	56·50	(*b*)
0·3987	,,	56·22	(*b*)
0·5062	,,	56·49	(*b*)
0·4255	,,	56·22	(*c*)
0·3682	,,	56·46	(*c*)
0·3763	,,	56·37	(*c*)
0·3717	,,	56·03	(*c*)
0·3344	,,	56·36	(*c*)
0·1725	0·2 eosin colour acid + 0·1 sodium chloride	56·39 56·36	(*c*)
0·1843	0·1 eosin colour acid + 0·1 potassium bromide	56·53	(*c*)
0·3309	0·4 sodium chloride	56·45	(*c*)

(*a*) The erythrosin colour acid used in these estimations was air dry.
(*b*) Alkaline fusion method.
(*c*) Permanganate oxidation method.

This procedure was applied to a number of commercial samples containing erythrosin in admixture with ponceau 3R and with amaranth, and in all cases a complete destruction of the organic matter and closely agreeing results were obtained.

It is believed that this method, with suitable modifications, is applicable to a number of other iodine compounds beside erythrosin, though detailed data substantiating this point have not yet been obtained. Iodine was determined in re-crystallised iodoform by first saponifying with alcoholic potash in a pressure flask, evaporating the alcohol, and oxidising the residue with permanganate as already given. The results are given in Table III. This procedure may be adopted with the class of compounds that are volatile and easily saponified, but obviously it need only be employed in cases where halogens other than iodine are also present.

Phenyl iodide, as a representative of another water insoluble class, was heated with the oxidising mixture in an acetylisation flask, the reaction mixture being in this case introduced through the tube of the reflux condenser, and boiled until the oily drops of phenyl iodide ceased to appear in the condenser, and then for some time longer, rinsing the condenser from time to time with a few cc. of the permanganate solution. The reaction mixture was removed from the flask and evaporated to dryness, proceeding from this point as in the case of erythrosin. These results also are given in Table III.

These determinations have not yet been checked against those obtained by other methods, but pending further work to establish the limits of usefulness of the procedure they are reported as found. The method seems to answer perfectly for the estimation of iodine in erythrosin, either when this colour alone is present or in a mixture with other colours, or with salts of the other halogens. Attention is called particularly to the results given in Table I., which hows the application of the method in inorganic analysis to the estimation of iodine in the presence of chlorides and bromides. The method seems to possess the double advantage of simplicity and accuracy.

TABLE III.—*Estimation of Iodine in Iodoform and in Phenyl Iodide.*

Grm. of substance used.	Iodine found, per cent.	
Iodoform (theory 96·7 per cent)—		
0·5922	95·90	(*a*)
0·4393	95·98	(*a*)
0·3097	95·80	(*b*)
0·4798	96·18	(*b*)
0·2435 + 0·3 sodium chloride	95·60	(*b*)
Phenyl iodide (theory 62·22 per cent)—		
0·3599	60·80	(*b*)
0·4042	60·61	(*b*)

(*a*) Saponification method.
(*b*) Permanganate oxidation method.

TIME, TEMPERATURE, AND COMPOSITION AS FACTORS IN SOFTENING WATER.*

By J. C. W. GRETH.

THE problem of softening and purifying water is much more difficult than at first appears to the novice.

The complexity of the impurities and the wide variations in waters from the same sources of supply do not admit of the application of a fixed method for all waters.

The softening of water is understood by many to be merely a question of the addition of lime and soda-ash. This is shown by articles in engineering and chemical journals and even government publications, advising the use of so much lime and soda-ash for a certain water supply. Looking at the problem from this point of view, the question naturally arises among engineers and water users as to the necessity of the apparatus for the proper softening and clarification of water.

In softening water we have to deal with extremely dilute solutions which are made complex by the number of substances in solution, each to some extent affecting the solubility of the other.

To remove the various salts of lime and magnesia from the dilute complex solutions by means of the two reagents, commercial caustic lime and soda-ash, both of which, especially the former, are likely to vary in purity, calls for an accurate method of control, and a wide experience with different waters.

Chemists usually estimate the quantity of reagents required on the basis of the molecular weights of the lime, magnesia, and iron salts in the water. It has been my experience that no fixed rules, applicable to all water supplies, can be laid down as to the exact quantity of reagents required, the method of controlling treatment, the time required for reactions and sedimentation, or for perfect clarification.

The time to be allowed for the complete softening of the water must be determined. No definite time can be set as being sufficient for all waters unless, of course, sufficient time is allowed in all cases to take care of those waters which require the maximum time for complete reaction.

This would hardly be practicable, as the cost of the water-softening system must be considered, and this cost is, in a large measure, dependent on the time allowed for reactions. In many types of water-softening apparatus on the market, the time allowed for reactions has been the uncertain minimum rather than the safe maximum.

That the time allowed for reactions is a question of vital importance, and that it has received little attention is evidenced by the fact that in many cases a softened water will leave the water-softening apparatus as it should, perfectly clear; but after standing for a time it becomes turbid, and eventually a deposit is found in the container. This can be seen in many of the track tanks of railroad

* Read before Pittsburgh Section of the American Chemical Society. —From the *Journal of Industrial and Engineering Chemistry*, iii., No. 1.

companies, or in the storage tanks of industrial plants, using water-softening apparatus. In some cases this becomes a serious annoyance and expense.

Again, deposits from softened water are found in feed-water heaters, and in pipe lines connecting the heater and boilers. Reference is not made here to a precipitate due to the reduced solubility of the lime and magnesia salts at the higher temperature, but to precipitation due to the continued reaction between the softening reagents and the lime and magnesia in the water. Moreover, sludge is deposited in the boiler. While this cannot be entirely prevented, yet in some cases the amount of sludge thrown down almost makes one believe that a boiler compound and unsoftened water had been used in place of a softened water. Again, it is extremely common in many water-softening systems to find even the pipe carrying the softened water from the system to be choked with scale. These effects are undoubtedly due to insufficient time for reactions within the softening apparatus.

Temperature is, of course, a factor in the time to be allowed, but in almost all cases it is desirable to soften the water before it is heated; therefore, the softening reactions must take place at temperatures between 32° and 85° F.

Every expedient known to the chemist and engineer must be employed in the design of apparatus to properly soften water on a large scale in a reasonable time. All chemists will agree that the addition of the reagents must be exact, and that they must be thoroughly mixed with the water. It would seem but rational to suppose that in the laboratory with a small sample, following the method employed on the large scale, ideal results could be obtained, and that these results might be used as a basis for designing water-softening apparatus, at least, as far as the time to be allowed for reactions is concerned, but let us see what actually occurs in attempting to treat a small sample of water in the laboratory, following as closely as possible the practice which gives results on the large scale.

The following analysis of a well-water with data showing the extent of the reactions for given periods of time has been selected from a large number of waters on which similar experiments have been tried to determine what can be done in the laboratory in attempting to parallel the results obtained on a large scale:—

	Parts per million.	Grains per U.S. gall.
Determinations.		
Volatile and organic matter	75	4·40
Silica	9	0·55
Iron and alumina oxides	trace	trace
Calcium oxide	158	9·30
Magnesium oxide	165	9·72
Sodium oxide	20	1·15
Sulphuric anhydride	343	20·20
Carbonic anhydride (fixed)	123	7·26
Carbonic anhydride (free)	none	none
Chlorine	12	0·70
Alkalinity as $CaCO_3$	281	16·50
Total solids by evap.	896	52·70
Probable Combinations.		
Volatile and organic matter	75	4·40
Silica	9	0·55
Iron and alumina oxides	trace	trace
Calcium carbonate	281	16·53
Calcium sulphate	2	0·10
Magnesium sulphate	496	29·16
Sodium sulphate	21	1·24
Sodium chloride	20	1·15
Total solids	904	53·13
Suspended matter	1	0·05
Free carbonic acid	none	none
Incrusting solids	788	46·34
Non-incrusting solids	41	2·39

The experiments on this water were made at temperatures ranging from 50° to 60° F. Under the heading "Boil," the sample had stood for twenty-four hours, then 100 cc. of it were brought to a boil, cooled, then filtered, and the determinations made.

Hours.	CaO. Parts per million.	CaO. Grains per U.S gallon.	MgO. Parts per million.	MgO. Grains per U.S. gallon.
1	51	3·00	53	3·10
2	26	1·50	10	0·60
3	26	1·50	10	0·60
4	17	0·98	5	0·30
24	14	0·84	5	0·30
Boil	10	0·56	3	0·20

These experiments were made on rather bad water, in fact water worse than the average. Now let us see the results of the same experiments on a water considerably better than the average, under a similar set of conditions, a river water.

	Parts per million.	Grains per U.S. gall
Determinations.		
Volatile and organic matter	9	0·55
Silica	8	0·45
Iron and alumina oxides	2	0·10
Calcium oxide	14	0·84
Magnesium oxide	3	0·18
Sodium oxide	1	0·07
Sulphuric anhydride	7	0·44
Carbonic anhydride (fixed)	7	0·44
Carbonic anhydride (free)	2	0·11
Chlorine	5	0·30
Nitric anhydride	2	0·10
Alkalinity as $CaCO_3$	17	1·00
Total solids by evap.	53	3·10
Probable Combinations.		
Volatile and organic matter	9	0·55
Silica	8	0·45
Iron and alumina oxides	2	0·10
Calcium carbonate	17	1·00
Calcium sulphate	11	0·68
Magnesium sulphate	1	0·06
Magnesium chloride	5	0·29
Magnesium nitrate	2	0·14
Sodium chloride	2	0·13
Total solids	57	3·40
Suspended matter	9	0·55
Free carbonic acid	2	0·11
Incrusting solids	47	2·72
Non-incrusting solids	2	0·13

Hours	CaO. Parts per million.	CaO. Grains per U.S. gallon.	MgO. Parts per million.	MgO. Grains per U.S. gallon.
1	39	2·30	3	0·20
2	39	2·30	3	0·20
3	39	2·30	3	0·20
4	39	2·30	3	0·20
22	36	2·10	3	0·20
Boil	33	1·96	3	0·15

From these experiments it would seem that at the end of two hours the treatment is practically completed. But the fact that a further reduction in both the calcium and magnesium oxides takes place after the end of two hours shows that the reactions are not entirely completed, and it is probable that just at this stage many water-softening machines stop in place of allowing sufficient time for the reactions to be completed.

The amount of impurity in the water is also a factor in the time to be allowed in softening a water This is illustrated by the second analysis ust cited. In s ex-

periment, after allowing twenty-two hours for the reactions to complete themselves, and heating the water to a boil, the total of the calcium and magnesium oxides is higher in the treated water than in the raw water, while in the first experiment the total of the calcium and magnesium oxides is lower in the treated water than in the raw water of the second experiment, showing that other factors besides time and temperature enter into the completeness of the softening.

As these experiments were conducted in exactly the same manner, and the conditions kept as nearly uniform as possible, one would have expected the results to be the same.

The results of such experiments, therefore, serve only as a guide which enables one having before him a large number of similar results, based on like experiments to draw conclusions, first, as to the length of time required on a large scale for complete reactions, and, second, as to the minimum to which the calcium and magnesium oxides can be reduced in the treated water.

After the time to be allowed for reactions has been determined, provision must be made for sedimentation and efficient clarification to carry the process to its logical conclusion, which is to remove the lime and magnesia as well as all suspended matter, to the extent that no after-precipitation can occur.

The following analysis shows a water very similar to the one cited for the second experiment :—

	Parts per million.	Grains per U.S. gall.
Determinations.		
Volatile and organic matter..	27	1·60
Silica	9	0·55
Iron and alumina oxides ..	2	0·10
Calcium oxide..	12	0·70
Magnesium oxide	5	0·32
Sodium oxide	21	1·24
Sulphuric anhydride	35	2·04
Carbonic anhydride (fixed) ..	4	0·22
Carbonic anhydride (free) ..	6	0·33
Chlorine	12	0·70
Nitric anhydride	trace	trace
Alkalinity as $CaCO_3$	9	0·50
Total solids by evap.	121	7·10
Probable Combinations.		
Volatile and organic matter..	27	1·60
Silica	9	0·55
Iron and alumina oxides ..	2	0·10
Calcium carbonate..	9	0·52
Calcium sulphate	17	1·00
Magnesium sulphate	16	0·96
Sodium sulphate	25	1·44
Sodium chloride	20	1·15
Total solids	125	7·32
Suspended matter	9	0·55
Free carbonic acid..	6	0·33
Incrusting solids	54	3·13
Non-incrusting solids	44	2·59

This water, after treatment with lime and soda-ash in a four-thousand gallon per hour water-softening system, in which a time of four hours is allowed for the softening, shows calcium oxide 9·5 parts per million; magnesium oxide, 1·4 parts per million; corresponding to calcium carbonate, 17 parts per million; magnesium hydrate, 2 parts per million; so here are two waters very much alike as to total hardness. One water under laboratory conditions is harder after treatment, allowing a longer time for reactions even with the aid of heat, while on a large scale a similar water is softened at atmospheric temperature, and in a much shorter time, to such an extent that both the calcium carbonate and the magnesium hydrate in the water are lower than the solubility of each of these substances in distilled water.

This is almost invariably the case, and proves that in a properly designed water-softening system a softer water can be obtained than by laboratory experiment conducted along correct scientific lines, paralleling as closely as possible the conditions existing in a regular softening system, even allowing more time for the reactions and with the aid of heat.

The time factor for the treatment of a particular water supply cannot therefore be directly determined by laboratory experiment, but must be found by a comparison of the experimental data with the results in practice.

The presence or absence of certain salts seems to have a direct bearing upon the time required for reactions and upon the solubilities of the calcium and magnesium compounds remaining in the treated water; but, so far, no reliable data are available that would warrant stating an opinion as to which of these salts cause this variation; nevertheless, the fact remains that the calcium and magnesium cannot be reduced to the same limits in all waters.

In some waters, at atmospheric temperature, the reactions are completed, and the water has settled perfectly clear at the end of two hours. In other waters, under the same conditions, and with the same type of apparatus, this result is not obtained until at the end of eight hours, and in some cases even a longer time. Therefore, in practice the time to be allowed is an important consideration, since the cost, as well as the extent of the softening, is dependent upon the time allowance for reactions and sedimentation.

Each water presents a specific problem that has to be worked out from the analysis, the experimental data, and the known results in practice with water of similar characteristics. In the absence of such data neither the results to be obtained can be accurately foretold, nor troubles avoided that follow imperfect softening.

It is, of course, true that any softening of the water is better than none, but by carefully considering the important factors which enter into the design of a water-softening system for a particular water supply, the additional outlay will be well invested, as there is a vast difference between the extent of softening obtained in many plants, due to improper design, and that which is obtainable with properly designed and operated apparatus.

REPORT ON CHEMICAL CONSTITUTION AND THE ABSORPTION OF LIGHT.*

By W. W. STRONG.

(Continued from p. 56).

Influence of the Solvent.

THEORETICALLY it would be expected that the position of the absorption bands would be different for different solvents. Kundt's rule that the bands should be shifted to the red as the refractive index increases does not hold. It is usually believed that the application of Kundt's rule is obscured by the formation of compounds between the dissolved compound and the solvent. The formation of such solvates seems to be quite definitely proven for some inorganic compounds and organic solvents (Anderson, *Phys. Rev.*, 1908, xxvi., 520; Jones and Strong, *Phys. Zeit.*, 1909, x., 499; *Journ. Am. Chem. Soc.*, 1910, xliii., 37, 97). Kauffman, Hantzsch and Glover, Gorke, Köppe and Staiger, and others, have recently shown that the extinction coefficient varies somewhat for every solvent. In the same solvent the extinction coefficient usually increases as radicals are added to the dissolved substance so as to increase its molecular weight. Hantzsch (*Ber.*, xlvi., 1556)

* This Report is based upon an article by H. Ley, entitled "Ueber die Beziehung Zwischen Lichtabsorption und Chemischer Konstitution bei Organischen Verbindungen." See *Jahrbuch der Radioaktivität und Elektronik*, 1910, vi., 274. From the *American Chemical Journal*, xliv., No. 1

gives evidence to show the presence of solvates and molecular aggregates in the case of nitrohydroquinone-dimethyl ether.

An interesting investigation has been made by Kalandek (*Phys. Zeit.*, 1908, ix., 128). Resonators will emit electro-magnetic waves of different wave-lengths, depending on the index of refraction of the liquid in which they are vibrating. Kalandek investigated the effect of different solvents on the period of various resonators, and also on the positions of the absorption bands of a large number of organic compounds. In general, the relations were not very close. It would be very interesting, however, to carry these investigations into the infra-red.

The Absorption Spectra of Benzene and its Derivatives.

Benzene and several of its derivatives show selective absorption in the ultra violet. Generally the absorption spectra of organic compounds consist of very wide diffuse bands. The absorption bands of gaseous benzene, on the other hand, are very fine. Benzene in solution shows seven absorption bands between λ 2330 and λ 2710, and in the gaseous state about thirty bands. Pauer (*Wied. Ann.*, lxi., 363), Friedrichs (*Zeit. Wiss. Phot.*, 1905, iii., 154), Grebe (*Zeit. Wiss. Phot.*, 1905, iii., 363), and Hartley (*Journ. Chem. Soc.*, 1900, lxxvii., 839; *Phil. Trans.*, 1908, ccviii., A, 475–528) have investigated several of the benzene compounds. The bands in the gaseous state are much finer and usually more numerous than in solution or in the solid state.

Both the vapour and solution bands are shifted to the red when the radicles Cl, Br, CH_3, &c., are substituted for hydrogen. The shift is generally greater the greater the molecular weight of the radical. The bands of benzene shifted in this way are the ones that are common to benzene, toluene, ethylbenzene, and hydroxyxylene, and are unaffected by temperature and pressure. Hartley gives the following wave-lengths for benzene:—

In solution.	As vapour.
λ.	λ.
2682	2670
2657—2642	2630
2614—2600	2590
2539	2523
2480	2466
2426·5	2411
2376	2360

As far as investigated, the substitution products o benzene have much less characteristic spectra than that of benzene itself. It would be very interesting to know whether the shift of the bands is gradual as the state is changed or as different chemical radicals are added.

Anthracene has the following bands:—

Solid.	Solution.	Vapour (fluorescent).
λ.	λ.	λ.
4250	4050	3900
4495	4275	4150
4745	4540	4320
4980	4820	—
5300	—	—

The substitution of saturated groups in benzene has been found to change the absorption spectra but little. Unsaturated radicals like NH_2, COOH, &c., change the spectra very greatly, so that there is hardly any relation to the benzene spectra. In the various di-substitution products the para compounds retain the characteristics of the benzene absorption better than the ortho or meta compounds. A considerable amount of work has been done by Hartley ("Handbuch. der Spectroscope," vol. iii.), Baly and Desch (*Journ. Chem. Soc.*, 1908, xciii., 1345, 1747, 1902), Ley and von Engelhardt (*Ber.*, xli., 2990), Baly and Collie (*Journ. Chem. Soc.*, lxxxvii., 1344), Ley (*Ber.*, xli., 1637), Hartley and Hedley (*Journ. Chem. Soc.*, 1907, xci., 319), Baly and Tuck (*Journ. Chem. Soc.*, 1908, xciii., 1902), and others, on the halogen, amino and nitro compounds of benzene, the phenols, pyridine, and its substitution products. A few of the results established will follow.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 26th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Memoir on the Theory of the Partitions of Numbers.* Part V. *Partitions in Two-dimensional Space.*" By Major P. A. MACMAHON, D.Sc., F.R.S.

"*Origin of Magnetic Storms.*" By ARTHUR SCHUSTER, F.R.S.

The paper contains a critical examination of the theory that magnetic storms are caused by streams of electrified corpuscles ejected from the sun. If the electro-kinetic energy of such storms be calculated, it is found that, when the magnetic field produced is comparable with that observed in magnetic storms, the energy is enormously great compared with that obtained by mere addition of the energies of the separate corpuscles. Even if during violent storms, when the magnetic force may be of the order 0·004 C.G.S., the corpuscles had an initial velocity nearly equal to that of light, the energy required to establish the magnetic field would be sufficient to reduce the speed to less than 4 kilometres a second before the swarm reaches the earth, the passage between the sun and the earth taking about a year. In this calculation the cross-section of the swarm is assumed to be determined by the effective duration of the magnetic disturbances which it is supposed to produce. If the swarm be reduced in cross-section the energy belonging to it would be diminished, but for a given magnetic force the density of the corpuscles in the swarm must then be correspondingly greater.

This leads to the consideration of the effects of electro-static repulsion between the particles. It appears that if H be the magnetic effect the electro-static acceleration at the edge of a swarm of electrons must be greater than 5×10^{17} H. This acceleration would be sufficient to drive a corpuscle in the first second through a distance equal to more than the diameter of the earth. It follows that, even taking account of electro-magnetic attractions between the corpuscles, a swarm of corpuscles, when sent out from the sun in a definite direction, would soon be dissipated to such an extent that no sensible magnetic disturbance could be produced. Finally, the electro-static effects, which would be observed on the surface of the earth in each magnetic storm, are discussed, and here the calculation also leads to the conclusion that the theory criticised is untenable.

If magnetic disturbances are produced by rays emanating from the sun, it can therefore only be in an indirect manner. We may imagine that the injection of corpuscles ionises the upper portions of the earth's atmosphere, and consequently renders the already existing electro-motive forces more effective, or we may imagine that the approach towards the earth's magnetic field of highly conducting material containing ions of both kinds acts by induction. The effect of such induction would primarily be an increase in the horizontal and a diminution of the vertical forces, while the currents induced in the earth, tending to diminish the horizontal forces, would, owing to their inertia, die out more slowly, so that a semi-permanent effect would be left after the storm. This agrees with observation, but there are at present not enough data available to test the sufficiency of the explanation.

"*Periodicity of Sun-spots.*" By Arthur Schuster, F.R.S.

In this communication, the sun-spots records of the last ten years are discussed in so far as they have a bearing on the results previously submitted to the Society. It appears that the period of 4·79 years discovered by the author is confirmed, but that the evidence does not support the periodicity of 4·38 years, which had been previously described as doubtful, nor that of 8·36 years, which during the first half of last century seemed active. Attention is drawn to the independent discovery of the period of 4·79 years in the declination range of the magnetic needle at Munich by Mr. Oppenheim.

"*Atmospheric Electricity over the Ocean.*" By G. C. Simpson, D.Sc., and C. S. Wright, B.A.

This paper contains the results of observations made on the voyage from England to New Zealand on Captain Scott's antarctic ship the "Terra Nova."

The investigation is divided into four parts. The first part deals with the electric potential-gradient over the ocean. It is found that the gradient has its chief maximum in the evening and its chief minimum soon after midday. The afternoon minimum is remarkable because, though observed at many stations on land, it has often been ascribed to the disturbing effect of dust. In view of the present results this explanation does not seem correct. The minimum, which is observed at 4 a.m., and which has been considered the principal one in observations taken on land, is only feebly developed at sea. The numerical value of the potential-gradient was found on the average to be about 80 volts per metre, and is therefore approximately the same as that observed on land.

The second part of the investigation deals with the quantity of radio-active products which are found in the air. The observations show that these products are decidedly less at sea than on land, and a specially low value both north and south of the equator is found in latitudes from 30° to 40°. This is ascribed to the fact that the air in these latitudes is supplied by pure air descending from the upper parts of the atmosphere, while it is mainly the air which has passed over land which carries radio-active products with it.

In the third part of the investigation the number of free ions in the air are measured, and here again it is found that the ionisation over the sea is smaller than that over land. In the concluding part of the paper the spontaneous ionisation in a closed vessel is measured. Though part of the effect is ascribed to a real effect of air becoming conducting by itself, some of the results obtained indicate clearly that when the ship near land was exposed to radio-active emanation the observed ionisation showed an increase for several hours afterwards.

"*The Fourier Constants of a Function.*" Dr. W. H. Young, F.R.S.

"*Energy and Distribution of Scattered Röntgen Radiation.*" By J. A. Crowther.

Experiments have been made to determine what fraction of the incident radiant energy is scattered per unit mass of a radiator when primary Röntgen rays fall upon it. From the numbers obtained a value has been deduced for the number of electrons per atom of the radiating substance. The value obtained agrees closely with that previously deduced from experiments on the scattering of homogeneous β-rays, being very nearly three times the atomic weight of the substance.

The distribution of the scattered radiation has been measured. It reaches a maximum forwards and backwards along the line of the primary beam, and falls to a minimum at right angles to this direction. At any given angle with the primary beam, there is always a preponderance of scattered radiation in the forward direction. This preponderance increases the more nearly we approach the line of the primary beam.

"*Some New Facts connected with the Motion of Oscillating Water.*" By Mrs. Hertha Ayrton.

The author's explanation of the origin of ripple-forming vortices having been contested, she has made further experiments to prove the two propositions on which it rests, viz., that when water oscillates over a submerged obstacle :—

1. During the whole of any single swing a diminution of pressure is established close to the upper part of the lee side of the barrier ;
2. While the water is falling below the mean level, in the half of the trough where the obstacle is, there is a back pressure against the flow on its lee side below the area of diminished pressure.

Experimental proof of these pressure conditions is given by means of an obstacle in the form of a hollow water-tight box, of which the top and one side are covered with thin guttapercha tissue diaphragms, the air being expelled, and the box partly filled with water.

These pressure conditions cause a jet to flow down close to the lee side of an obstacle during the first part of a swing, and a vortex to form during the second by upsetting the equilibrium of water, in the lee of the obstacle, that would otherwise remain at rest. The back pressure extends only to the limits of this slack water, *i.e.*, to the line where the lowest water flowing over the obstacle strikes the bottom.

A trough with an artificial end fitted with diaphragms is used to show that such pressure conditions are not confined to submerged obstacles, but come into existence close to any solid where water, in oscillating, is moving away from it ; and wherever two masses of water are flowing away from one another, as at the node of a stationary wave.

These variations of pressure give rise to jets and vortices near the surface of oscillating water, wherever it meets the end of a vessel, and at every node ; it is these jets and vortices, and the streams that feed them, that cause the residual whirls previously found by the author in oscillating water. The most important proof of this is that when the trough is rocked, so that there is much bottom motion but very little rise and fall, and, consequently, only feeble jets and vortices, the author's residual whirls are insignificant, while Lord Rayleigh's, beneath, develop to their full length and height, even in deep water.

CHEMICAL SOCIETY.

Ordinary Meeting, January 19th, 1911.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. Henry Dent Gardner, jun., and Thomas R. Merton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Ewart Trounce Barbary, Vallansaundry, near Camborne ; Harold Christopher, B.Sc., Mona, Lucien Road, Tooting Common, S.W. ; Harold Edgar Dryden, 490, Stanton Road, Burton-on-Trent ; James Furnival Eardley, Elmsdale, Broomhall Park, Sheffield ; William Joseph Chetwynd Horne, care of Messrs. Cleeve Bros., Lansdowne, Limerick ; Reginald Hurst, 50, Culverley Road, Catford, S.E. ; James William MacBain, M.A., Ph.D., 71, Cotham Brow, Bristol ; Edward Partington, Oakdene, Sedgley Park, Manchester ; Cyril James Peddle, M.Sc., 146, Barnsley Road, Cudworth, near Barnsley ; David Thomson, M.A., B.Sc., Ph.D., Viewpark, Litham Road, Strathaven, N.B. ; William Denham Verschoyle, 15, Winch Building, Vancouver, B.C. ; Bertie James Waygood, 39, Marshall Road, Levenshulme, Manchester ; Edward Escott Wood, Hurricane House, Brymbo, N. Wales ; Charles Fursdon Yates, Ronaldene, Witham Road, Isleworth,

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Solomon Farley Acree, Johns Hopkins University, Baltimore, Md., U.S.A.; Robert Leonard Emerson, A.B., M.D., Boston, Mass., U.S.A.

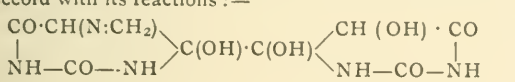
Of the following papers, those marked * were read :—

*1. "*The Interaction of Alloxan and Glycine.*" By WILLIAM HOLDSWORTH HURTLEY and WILLIAM ORD WOOTTON.

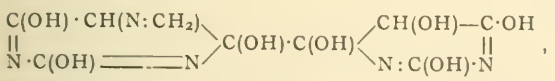
The authors have examined the action of alloxan on glycine in aqueous solution. By mixing concentrated solutions of these, Piloty and Finkh (*Annalen*, 1904, cccxxxiii., 22) isolated a substance which they described as glycine purpurate. The authors regard this product as a mixture of at least three substances. They have examined the action as it occurs in dilute solution on heating, and, unlike Strecker (*Annalen*, 1862, cxxiii., 363) and Piloty and Finkh (*loc. cit.*), find that formaldehyde is evolved. The reaction occurs in several stages, murexide being produced first, then a substance closely related to uramil, and finally a substance isolated by Piloty and Finkh and regarded by them as uramidoacetic acid. This, the main product of the reaction, is a pale yellow crystalline solid, characterised by powerful reducing properties, by yielding formaldehyde on hydrolysis or by treatment with 50 per cent nitric acid, by the production of an amide with ammonia, and by the formation of alloxan with dilute nitric acid. The authors are of the opinion that a substance possessing these properties cannot have the formula—

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH.NH\cdot CH_2\cdot CO_2H,$$

which is assigned to it by Piloty and Finkh; they give it therefore the following constitution, which is more closely in accord with its reactions :—



or—



and propose to name it 2 : 4 : 6 : 2′ : 4′ : 5′ : 6′-*heptahydroxy*-5-*methyleneamino*-4 : 5 : 4′ : 5′-*tetrahydro*-4 : 4′-*dipyrimidyl*.

DISCUSSION.

Dr. HURTLEY, in reply to Dr. Pyman, stated that the yield of formaldehyde in this reaction was 7·5 per cent of the theoretical.

*2. "*Intramolecular Re-arrangements of Diphenylmethane* o-*Sulphoxide.*" By THOMAS PERCY HILDITCH and SAMUEL SMILES.

Diphenylmethane *o*-sulphoxide (I.) is obtained by the oxidation of thioxanthen with hydrogen dioxide, and it is converted into the red carbothionium chloride (II.) by the action of hydrogen chloride—

$$C_6H_4<\begin{matrix}CH_2\\SO\end{matrix}>C_6H_4 \qquad\qquad C_6H_4\equiv\begin{matrix}CH\\SCl\end{matrix}>C_6H_4$$

I. II.

in dry alcohol. This salt is more readily obtained from thioxanthenol with hydrogen chloride in ethereal solution, and, if excess of hydrochloric acid is removed, it is transformed into thioxanthenyl chloride, $C_6H_4<\begin{matrix}CHCl\\S\end{matrix}>C_6H_4$. Thioxanthenol is regenerated from the latter substance or from the carbothionium salt by the action of water or alkaline reagents. The transference of oxygen from sulphur to carbon, which may be effected by thus converting the sulphoxide into thioxanthenol, may be carried out by the aid of heat alone, for both substances furnish thioxanthenyl oxide when they are heated to about 120°.

This re-arrangement was discussed from a general point of view, and in its bearing on the behaviour of the analogous diphenylamine *o*-sulphoxide.

*3. "*The Reactions between Chemical Compounds and Living Muscle-proteins.*" By VICTOR HERBERT VELEY.

The main conclusions drawn by the author are as follows :—

1. When a living muscle is immersed in solutions of certain compounds, a chemical change takes place between the solute and the amino-acids formed from the muscle-proteins by hydrolysis; its rate can be measured by the height of response to induction shocks used as an indicating record.

2. In most cases examined, the rate of change is a logarithmic function of time represented by the equation of a reaction of the first order, namely, $K = 1/t(\log r_0/r_t)$, in which r_0 is the number of units of potential chemical change, when $t = 0$, and r_t the number of units remaining after expiry of time t.

In a few cases the rate of change is a linear function of time, which, although less conclusive, does nor exclude the possibility of a chemical change.

If the hypothesis be correct that the chemical changes are due to a reaction between the drug, whether acid or base, and the amino acid, either formed by hydrolysis of the muscle-proteins or present by virtue of the moribund condition of the muscle, then amino-acids should produce no change, or, in other words, the record would not differ from that of a fatigue effect. Results were given in the case of aminoacetic acid in proof of this line of argument.

4. "*The Decomposition of Tetramethylammonium Nitrite by Heat.*" By PRAFULLA CHANDRA RAY and HEMENDRA KUMAR SEN.

Tetramethylammonium nitrite decomposes at 228—230°, but more regularly and rapidly at 250—260°. The main gaseous products of decomposition are trimethylamine, methyl nitrite, carbon dioxide, nitric oxide, nitrogen, and water. A small fraction of the salt at the same time undergoes charring with the formation of an oily liquid which soon becomes resinified.

5. "*Influence of Minute Quantities of Ferric Salts and of Manganese Nitrate on the Rate of Solution of Mercury in Nitric Acid.*" By PRAFULLA CHANDRA RAY.

Minute quantities of ferric nitrate (0·026 grm.) or ferric sulphate (0·0025 grm.) in dilute nitric acid (50 cc.) containing 12 to 13 per cent of the acid have a marked retarding effect on the dissolution of mercury in it.

Manganese and sodium nitrates, on the other hand, accelerate the dissolution of mercury in nitric acid.

6. "*On* dl- *and* d-Δ^2-m-*Menthenol*(8) *and* dl- *and* d-$\Delta^{2:8:(9)}$-m-*Menthadiene.*" By WALTER NORMAN HAWORTH, WILLIAM HENRY PERKIN, jun., and OTTO WALLACH.

An account was given of the synthesis of the substances mentioned in the title, and of many of their derivatives, by two different methods. The physical properties of all these substances have been determined, and were fully discussed.

7. "*The Identity of Xanthaline and Papaveraldine.*" By BESSIE DOBSON and WILLIAM HENRY PERKIN, jun.

The authors have made a careful study of the alkaloid xanthaline, which Messrs. T. and H. Smith, *Pharm. Journ.*, 1893, p. 793) isolated in very small quantities from opium, and they find that this alkaloid is identical with papaveraldine.

8. "*Amalgams containing Silver and Tin.*" By REGINALD ARTHUR JOYNER.

The non-existence of any compound of silver with tin other than Ag_3Sn is confirmed. The "ageing" of filings of silver-tin alloy has been experimentally verified and investigated. The composition of saturated liquid amalgams of tin, of silver, and of tin with silver has been determined at a number of temperatures, and the equilibrium diagram representing the ternary systems existing below

63° has been ascertained. No ternary compound exists at these temperatures, and the stable solid phases are the compound Ag_3Hg_4 and a solid solution containing a small amount of mercury dissolved in tin. No solid solution exists between these two solid phases. The alloys of silver with tin are thus completely decomposed by the action of excess of mercury. At higher temperatures a ternary compound is formed.

9. "*Studies of the Constitution of Soaps in Solution. The Electrical Conductivity of Sodium Stearate Solutions.*" By Richard Charles Bowden.

At 90° the equivalent conductivity of sodium stearate in aqueous solution is about half that of sodium acetate, being 88·3 ohms in a weight-normal solution, about 77 for solutions between N/2- and N/20-, but rising to 125·9 in N/100-solution. It is considered that these measurements demonstrate the presence of a high concentration of free electrolyte in solutions of sodium stearate. The change in conductivity with the dilution differs from that in solutions of sodium palmitate, but it is not less remarkable. Attention was drawn to the connection between these phenomena and the analogous behaviour of certain non-aqueous solutions as well as to the salting out from soap solutions of acid sodium salt by means of concentrated solutions of sodium hydroxide.

10. "*Additive Compounds of Phenols and Phenolic Ethers with Aromatic Polynitro-derivatives.*" By John Joseph Sudborough and Stanley Hoskings Beard.

The authors described a number of additive compounds prepared from *s*-trinitrobenzene and phenols, phenolic ethers, and cyclic oxygen derivatives. Many of the compounds are coloured, but as a rule are much paler than the additive compounds of amines and *s*-trinitrobenzene.

11. "*The Effect of Contiguous Unsaturated Groups on Optical Activity.* Part VI. *The Influence of the Carbonyl Group on Optical Rotatory Power.* Part VII. *The Relative Influences of Aromatic and Hydroaromatic Nuclei on Optical Rotatory Power.* Part VIII. *The Influence on Optical Activity of Two Contiguous Unsaturated Groups in Comparison with that of One Unsaturated Group at varying Distances from the Optically Active Complex.*" By Thomas Percy Hilditch.

1. The author has sought to obtain evidence of the effect of the system $\cdot CO\cdot CO_2H$ on optical rotatory power, in order to effect a comparison with that of the group $\cdot CH{:}CH\cdot CO_2H$, which is now fairly well known.

From investigation of the menthyl esters and brucine salts of ketonic acids of the pyruvic, mesoxalic, and phenylglyoxylic series, it appears that the carbonyl group increases the initial effect of the carboxyl group on the molecular rotatory power of the optically active alcohol or acid, and its influence is thus very similar to that of an ethenoid bond.

2. The relative influences of aromatic and hydroaromatic nuclei on optical activity have been investigated by means of the salts formed from corresponding aromatic and hydroaromatic bases with optically active acids (camphoric, camphor-π-sulphonic, and tartaric acids). The results show consistently that so long as an aromatic group is contiguous to the basic nitrogen atom, a well-defined optical anomaly persists, but this disappears wherever the radicle attached to the nitrogen is fully reduced. It was also pointed out that "ring-formation," which is usually stated to produce a large alteration in rotatary power, does so only when the asymmetric carbon atoms form part of the ring system.

3. Rupe (*Annalen*, 1903, cccxxvii., 157) has stated that the nature of the effect of unsaturated groups on optical activity is determined by their nearness to the asymmetric atoms. Experiments have been carried out to decide whether, in certain cases, it is the proximity of an unsaturated system to the asymmetric complex, or the conjugated unsaturated groups present, which causes the anomaly in rotatory power, and it appears that whilst both causes undoubtedly operate, the latter is the more powerful factor.

12. "*The Relative Effects of Ethylenic and Acetylenic Linkings on Optical Rotatory Power.*" By Thomas Percy Hilditch.

d-*Methylhexylcarbinyl β-phenylpropionate*, *cinnamate*, and *phenylpropionate*, and the neutral and acid *menthyl* esters of *succinic*, *fumaric*, and *acetylenedicarboxylic acids* have been examined with respect to the relative effects of the ethylenic and acetylenic linkings on optical rotatory power; the former series is interesting in view of the simplicity of the asymmetric system in the alcohol used and the similarity of this compound to amyl alcohol.

From a general survey of the fourteen series of active salts or esters of these acids now available for comparison, it is seen that in twelve cases the fully saturated member is least anomalous in optical activity, whilst in the other two the ethylenic and acetylenic compounds respectively possess the smallest rotatory power. On the other hand, it is concluded that there is no general rule to cover the relative effects of the double and triple carbon linkings, and that the influence of the acetylenic (+carboxyl) residue is in general much less well defined than that of the ethenoid (+carboxyl) group.

13. "*The Direct Action of Radium on Ammonia.*" By Edgar Philip Perman.

The rate of decomposition of ammonia by the direct action of radium bromide has been measured approximately. The pressure of the ammonia, together with its decomposition products, decreased for five weeks, and then steadily increased. The reaction appears to be of the first order.

14. "*Cupritartrates and Analogous Compounds.*" By Spencer Umfreville Pickering.

By adding potassium hydroxide to copper tartrate just short of alkalinity, and precipitating by alcohols, a cupritartrate of the formula $(C_2H_4O_2\cdot CuO)_2(CO_2)_4K_2Cu,H_2O$ is obtained, and by the further action of the alkali and water, two others derived from this by the partial substitution of copper for the potassium were also prepared. Analogous compounds of saccharic and mucic acid were obtained, $(C_4H_8O_4\cdot CuO)_2(CO_2)_4K_2Cu,H_2O$, as also was an *α*-cupritartrate, $(C_2H_4O_2\cdot CuO)_4(CO_2)_8K_4Cu_2,(CuCO_3)_2,Na_2CO_3$. All six compounds, when dried at a temperature just below that at which they decompose, gave minimum molecular weights agreeing with these formulæ, and inconsistent with the view that the copper displaces the hydrogen in the alcoholic hydroxyl. Probably this hydrogen is displaced by the group $(Cu^{II}OH)^{I}$, the copper in the carboxylic portion of the molecule being present as $(Cu^{IV}O)^{II}$, as in the cupricitrates. Quinic acid forms analogous compounds, but these were not obtained in a pure condition.

15. "*Molecular Association in Water.*" By Cyril James Peddle and William Ernest Stephen Turner.

Following on the work of Meldrum and Turner, which revealed the existence of molecular association in water of a number of amides and anilides (*Trans.*, 1908, xciii., 876; 1910, xcvii., 1805), it was shown that molecular association in water is of frequent occurrence. A number of carboxylic acids, phenols, and amines have now been examined. Except in the case of the aliphatic amines, most of the substances are distinctly associated. Benzoic acid is more associated in water than in benzene. The appearance of water among the solvents which permit association so contrary to the general experience and belief in its dissociating power, was explained on the supposition that molecular association in water is really due to a dissociation of complex water molecules, a view suggested in connection with the amides, and now further developed and applied to other associated solvents.

16. "*Note on the Preparation of Thiobenzanilide.*" By Edward de Barry Barnett.

Thiobenzanilide can readily be obtained in 90 per cent yield by the following modification of Bernthsen's method (*Ber.*, 1878, xi., 503):—Twenty grms. of benzanilide are intimately mixed with 10 grms. of finely ground phos-

phorus pentasulphide and 10 grms. of finely ground phosphorus trisulphide. The whole is then cautiously heated over a naked flame with continual shaking until fusion takes place. After cooling, the mass is extracted several times with boiling acetone or alcohol, the united extracts rendered strongly alkaline with sodium hydroxide, and then poured into a large bulk of water. The dark solution obtained on filtration is then saturated with carbon dioxide, when the thioanilide is obtained as a yellow crystalline precipitate, which need not be further purified.

Attempts to apply the above method to the preparation of thioformanilide and thioacetanilide were not successful, owing to the large quantity of tarry matter formed.

17. "*Organic Derivatives of Silicon.* Part XIV. *The Preparation of Tertiary Silicols.*" By Frederic Stanley Kipping and John Edward Hackford.

Tertiary silicols, $R_3Si{\cdot}OH$, can be prepared by treating silicones, R_2SiO, with a Grignard reagent; termolecular silicones, $(R_2SiO)_3$, dihydric silicols, $R_2Si(OH)_2$, and substituted metasilicic acids, $R{\cdot}SiO{\cdot}OH$, may also be employed for this purpose.

The following compounds were prepared:—*Benzyldiethylsilicol*, $SiEt_2(CH_2Ph){\cdot}OH$; *benzylethylpropylsilicol*, $SiEtPr(CH_2Ph){\cdot}OH$; *phenylmethylethylsilicol*, $SiMeEtPh{\cdot}OH$; *phenyldiethylsilicol*, $SiEt_2{\cdot}Ph{\cdot}OH$; *dibenzylmethylsilicol*, $SiMe(CH_2Ph)_2{\cdot}OH$; *triphenylsilicol*, $SiPh_3{\cdot}OH$; *tribenzylsilicol*, $Si(CH_2Ph)_3{\cdot}OH$. When phenylsilicon trichloride is treated with steam, it gives the anhydride of phenylmetasilicic acid, whereas with water it gives the acid. The anhydride is insoluble in all neutral liquids which were tried, and is probably highly polymerised.

18. "*o-Carboxyanilides of the Sugars.*" By James Colquhoun Irvine and Alexander Hynd.

The conditions under which the common reducing sugars condense with anthranilic acid have been ascertained, and it is found that the best results are obtained when solutions of the sugars in dilute alcohol are mixed with excess of the acid and kept in the cold for several weeks. In this way, *galactose*, *mannose-*, *rhamnose-*, and *maltose-o-carboxyanilides* have been prepared. Lactose gave a negative result. In the case of fructose, the product could not be obtained pure, and the corresponding glucose compound has already been prepared (*Trans.*, 1909, xcv., 1553).

The condensation proceeds by reaction between the amino-group and the reducing group of the sugar, as all the products behave as acids. The compounds appear to be γ-oxides, as they show extremely rapid mutarotation comparable in magnitude and direction with that given by anilides and methylated anilides.

Glucose also condenses with alanine in a similar manner to give *glucosealanide* (m. p. 114°), which, judging from its optical behaviour, exists in α- and β-forms, which are interconvertible at 90°.

A parallel investigation carried out with tetramethyl glucose shows that reaction does not proceed readily between amino-compounds and the methylated sugar, and even ammonia and hydrogen cyanide are without action in the cold. *Tetramethyl glucose-p-phenetidide*, *-β-naphthylamide*, and *p-toluidide* were, however prepared. The latter alone is crystalline (m. p. 144°), and shows extensive mutarotation.

19. "*The Iodobenzenemonosulphonic Acids.* Part III. 2 : 3-*Di-iodo-* and 2 : 3 : 4 : 5 *Tetraiodo-benzenesulphonic Acids.*" By Mary Boyle.

2 ; 3-*Di-iodobenzenesulphonic acid* has been prepared by treating *p*-nitroaniline-*o*-sulphonic acid with iodine chloride, the nitro-group being removed after the displacement of the amino-group by iodine. A new and convenient method of obtaining the initial nitroamino-acid in large quantities has been devised.

The di-iodosulphonic acid separates from mineral acid solutions in shining crystals, and yields crystalline salts and a well-characterised *chloride*; its *methyl* and *ethyl* esters have been prepared. The *tetraiodo-acid* is prepared from *m*-iodoaniline-*p*-sulphonic acid; its *chloride* differs from those containing two or three iodine atoms in possessing a distinct yellow colour.

20. "*Occurrence of Pentathionic Acid in Natural Waters.*" By James Scott Maclaurin.

Pentathionic acid has not previously been found in natural waters. This may be due to the fact that in ordinary analyses of mineral waters no special search is made for such compounds. Some account of the circumstances that led to the discovery of the occurrences of the acid should therefore be of interest.

The water in which it was found was obtained from a lake on White Island. This island, which is the summit of a volcano, lies in the Bay of Plenty about thirty miles from the mainland. The lake covers an area of approximately 15 acres, and has a mean temperature of about 110° (Fahr.). The water is of a very unusual character, containing a great variety of salts and much free hydrochloric acid. In examining it for iodine by the potassium nitrite test, the author noticed the formation of a brown colour, which suggested the presence of a ferrous salt, but, on titrating with potassium permanganate, more permanganate solution was used than the iron (previously determined gravimetrically) could require, even if all were in the ferrous state, and judging by the colour of the water, much of the iron was in the ferric state. There was no organic matter to cause this excessive reduction, and on adding N/10-iodine solution no appreciable action took place, showing that the reduction could not be caused by sulphur dioxide or hydrogen sulphide. After removing sulphates by means of excess of barium chloride, and heating the filtrate with bromine water, a further precipitate of barium sulphate was formed, showing that some sulphur compound was present. It seemed probable that this was one or more of the polythionic acids, most probably pentathionic acid. In order to prove the truth or otherwise of this surmise, the water was boiled with mercuric cyanide (Debus, *Trans.*, 1888, liii., 278). The reaction between mercuric cyanide and pentathionic acid is as follows:—$Hg(CN)_2 + H_2S_5O_6 = HgS + S_2 + 2SO_3 + 2HCN$. If the mercury in the precipitate ($HgS + S_2$) be determined, the equivalent amount of hydrogen in the pentathionic acid can be calculated, and, by precipitating the SO_3 in the filtrate as barium sulphate, the oxygen and part of the sulphur can be estimated. The remainder of the sulphur can be determined in the first precipitate ($HgS + S_2$). The results so obtained approximated roughly to the formula $H_2S_5O_6$. The value for oxygen was, however, too high, and it was thought probable that this was due to the oxidising action of the ferric chloride and hydrogen chloride present in considerable quantities in the water. Attempts to remove these substances by the ordinary methods were unsuccessful, but the difficulties were met by shaking the water with slightly less magnesium oxide than was necessary to neutralise the free acid, and then precipitating the iron with potassium ferrocyanide.

Although the hydrochloric acid could be nearly neutralised by this means, the chlorides so formed reacted with the mercuric cyanide, so that instead of a precipitate of the composition $HgS + S_2$, one containing a large proportion of mercuric chloride was obtained. This rendered the determination of the hydrogen in the pentathionic acid more difficult and less trustworthy than in the absence of mercuric chloride. It was therefore decided to be satisfied with the approximate values for hydrogen already found, but to redetermine the sulphur and oxygen.

For this purpose 2000 cc. of the water were precipitated in the cold with slightly less barium chloride solution than was necessary to throw down all the SO_3. After twenty-four hours, the barium sulphate was collected, and the filtrate was divided into three portions, A, B, and C. In A, the small amount of SO_3 still remaining was estimated by adding excess of barium chloride, and keeping for twenty-four hours. This determination was made in the cold, because boiling causes slight decomposition of pentathionci

acid. In B, the total sulphur was determined by oxidising with bromine water and precipitating with barium chloride. C was boiled with mercuric cyanide, the precipitate collected, and the SO_3 in the filtrate determined by boiling with solution of barium chloride. By subtracting the amount of barium sulphate obtained in A from the amounts found in B and C respectively, the sulphur and oxygen of the pentathionic acid were readily calculated. The results so obtained gave $S_5O_{5\cdot92}$.

The complete analysis of the water, in percentage composition, is as follows:—

SiO_2	0·0080
TiO_2	0·0030
SO_3	2·6534
CO_2	0·0130
P_2O_5	nil
B_2O_3	0·0310
As_2O_3	0·00056
Cl	4·8210
Br	0·0034
I	trace
O (basic)	0·5306
Fe	0·1456
Mn	0·0014
Al	0·3330
Ca	0·1497
Mg	0·0790
K	0·0884
Na	0·2154
Mo	trace
Cu	,,
NH_4	0·0091
H (in HCl)	0·1328
$H_2S_5O_6$	0·0240
	9·24236

These results may be re-stated as follows;—

NH_4Cl	0·0273
KCl	0·1654
NaCl	0·0379
KBr	0·0051
KI	trace
Na_2SO_4	0·6191
$MgSO_4$	0·3948
$CaSO_4$	0·5090
$Al_2(SO_4)_3$	2·1090
$Fe_2(SO_4)_3$	0·2600
$FeSO_4$	0·1976
$MnSO_4$	0·0038
$CuSO_4$	trace
MoO_3	,,
SiO_2	0·0080
TiO_2	0·0030
B_2O_3	0·0310
As_2O_3	0·00056
CO_2	0·0130
HCl	4·8338
$H_2S_5O_6$	0·0240
	9·24236

21. "*β-Methyl-$\Delta^{\alpha\lambda}$-Dodecadiene and β-Methyl-$\Delta_{\alpha\gamma}$-decadiene.*" By Victor John Harding, Gertrude Maud Walsh, and Charles Weizmann.

An account was given of the preparation of the above mentioned hydrocarbons from the corresponding tertiary ohols:—

$CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CMe_2{\cdot}OH \rightarrow$
$\rightarrow CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CMe{:}CH_2.$

$CH_3{\cdot}[CH_2]_5{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}OH \rightarrow$
$\rightarrow CH_3{\cdot}[CH_2]_5{\cdot}CH{:}CH{\cdot}CMe{:}CH_2.$

22. "*Determination of the Vapour Pressures of Hydrates by a Dynamical Method.*" (Preliminary Note). By James Riddick Partington.

The vapour pressures of copper sulphate hydrate ($CuSO_4,5H_2O$) and racemic acid hydrate have been determined by comparing the amounts of water removed from the hydrate, and from pure water by a stream of air in a special apparatus.

The values in the first case are higher than the tensimetric (static) values; in the latter case, the vapour pressures exhibit a maximum with respect to extent of dehydration as independent variable. Both phenomena are found to be mathematical consequences of the initial formation of an unstable lower hydrate, or unstable anhydrous substance, which passes slowly into a stable form.

23. "*A Simple Demonstration of Gibbs's Phase Rule.*" By James Riddick Partington.

The proof of the phase rule given by Gibbs (*Scientific Papers*, i., pp. 62—100) is far too difficult to present to beginners in physical chemistry, and the following much simplified exposition of Gibbs's original demonstration has been found quite intelligible to students, and may be useful to teachers.

The assumption is made that it is possible to have a state of equilibrium between several phases at a definite temperature and pressure; this will be characterised by certain definite relations between the compositions of the phases (for example, a solid salt, saturated solution, vapour of the solvent).

Let p, θ = total pressure and temperature of the system.
n = number of components.
r = ,, phases.

For each pair of phases there must be some condition satisfied for each component, such that this particular component does not pass from one phase to the other. The r phases may now be arranged in $(r-1)$ pairs, namely, $(1, 2)$, $(2, 3)$, $(3, 4)$, . . $\{(r-1), r\}$, and there will therefore be $(r-1)$ conditions to be satisfied for each component in all the phases; that is, $(r-1)$ equations defining the equilibrium. It is evident that such pairs as $(1, 3)$, $(2, 4)$, &c., need not be considered, since, if phase (1) is in equilibrium with phase (2), and phase (2) with phase (3), then (1) will also be in equilibrium with (3). If this were not the case, we could, by enclosing (1), (2), (3) in a ring-shaped tube, so that there are three surfaces of separation, set up a continuous circulation at a uniform temperature, which is contrary to the second law of thermodynamics.

For all the components there will therefore be $n(r-1)$ equations.

The number of variables is made up of:—
(i.) The pressure p.
(ii.) The temperature θ.
(iii.) The number of concentrations $= r(n-1)$, since for each phase we have $(n-1)$ fractions of the total mass for the n components, the last (nth) fraction, being obtained by subtracting the sum of all the others from the total mass, is fixed, and is not an independent variable, therefore—

$$\text{Number of variables} = 2 + r(n-1).$$

The number of variables left undetermined—

$$= \text{Number of variables} - \text{number of equations}$$
$$= 2 + r(n-1) - n(r-1)$$
$$= 2 + n - r.$$

This, however, is defined as the number of degrees of freedom (F) of the system, hence:—

$$F + r = n + 2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a).$$

If any component is absent from a particular phase (for example, the vapour phase, or a solid phase), there is one variable less, but also one boundary condition less, for migration of that component cannot occur with respect to the phase considered. The equation (a) is therefore still true.

24. "*Cholesterol and Fatty Acids.*" By James Riddick Partington.

The solids separating from a fused mixture of cholesterol

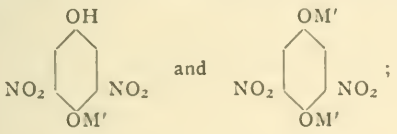
with palmitic, stearic, or oleic acid are found, by an examination of the freezing-point curves, to be either pure substances, or mechanical mixtures of these substances, and not compounds, as has been previously assumed.

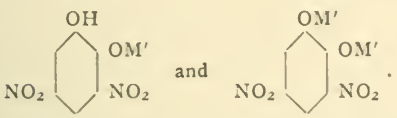
25. "*Salts of the Dinitrodihydroxybenzenes.*" By William Bayliss Shaw.

Although the dinitrodihydroxybenzenes have been known for some years, no systematic investigation of their salts has been carried out.

The author has prepared a complete series of the alkali-metal salts of 3 : 5-dinitroquinol, 3 : 5-dinitrocatechol, and 4 : 6-dinitroresorcinol by the addition of an alcoholic solution of the metallic hydroxide to the nitro-compound dissolved in an indifferent solvent, such as ether.

In the case of the quinol and catechol derivatives, two series of salts have been prepared, having the formulæ :—

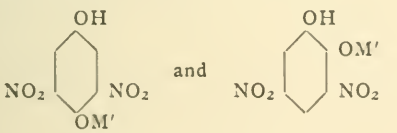




Only the neutral salts of dinitroresorcinol have been obtained.

A sharp colour distinction exists in the quinol and catechol series between the neutral and acid salts.

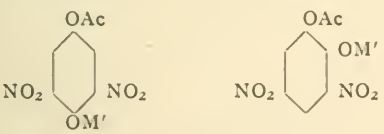
The acid salts of the forms—



are all of an orange or red tint, whilst the neutral salts are almost black.

The neutral salts of dinitroresorcinol resemble the acid salts of the other two series, no darkly coloured substances having been found.

It has also been possible to prepare, although not in a high degree of purity, salt of the formulæ :—



by employing the dinitro-diacetate in place of the free nitro-compound, since one of the acetyl groups is much more easily removed than the other.

By acting on a neutral salt with methyl sulphate, the corresponding monomethyl ether can be obtained. The introduction of two methyl groups by this means has not been accomplished

All attempts to methylate 4 : 6-dinitroresorcinol with methyl sulphate have failed.

Some fifty new salts have been prepared, and it is hoped to publish full details shortly.

Royal Institution.—Prof. Karl Pearson being unable to lecture at the Royal Institution on March 3, the Friday Evening Discourse on that date will be delivered by Dr. F. A. Dixey, his subject being "Scents of Butterflies."

CORRESPONDENCE.

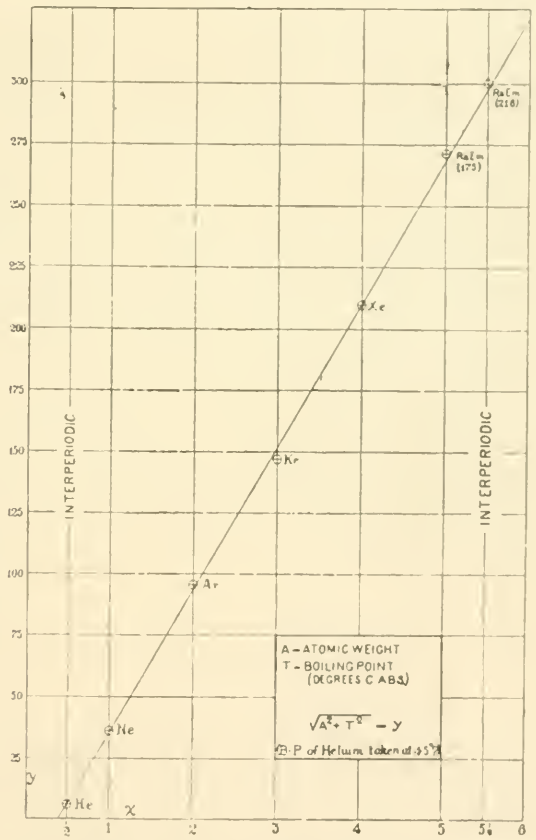
PHYSICAL PROPERTIES OF INACTIVE GASES.

To the Editor of the Chemical News.

Sir,—Referring to some of the physical properties of the inactive gases, may I allude to a tendency of those of high atomic weight to show departures from a regular series when their atomic weights are introduced into the calculation. They may thus behave experimentally as if they were gases of lower atomic weight. In some cases this points to the probable necessity of taking into account a third factor or condition in the formula, in order that values may be selected which are physically or legally comparable.

The following is an example :—

A. v. Antropoff (*Proc. Roy. Soc.*, Series A, lxxxiii., 474, April 14, 1910) has determined the solubilities of the



inactive gases in water at different temperatures. At 20° C. he arrives at the following results :—

He	= 0·0138	Kr	= 0·0670 / 0·0788
Ne	= 0·0147		
Ar	= 0·0379	Xe	= 0·1109

If these solubilities are multiplied by the corresponding atomic weights, taking a mean value for the solubility of krypton, the following figures are obtained :—0·055, 0·294, 1·511, 6·045, 14·5.

Representing these values as rounded-off figures (multiplied by 10 to avoid a repetition of fractional parts) the following regularity appears :—

$$6 \times \tfrac{1}{2} = 3$$
$$5 \times 3 = 15$$
$$4 \times 15 = 60$$
$$3 \times 60 = 180 \text{ } \textit{instead of 115}$$

As in the case of Bode's law, the last number shown is not in agreement with the value based upon experiment. According to this method, the series would indicate the existence of two inactive gases of greater atomic weight than xenon.

The solubility of radium emanation in water as determined by R. Hofmann (*Phys. Zeit.*, 1905, vi., 337) at 20° C. is 0·23, this being the absorption coefficient. A later determination by M. Kofler (*Phys. Zeit.*, 1908, ix., 6) is of the same order, namely, 0·27 at 18° C. A continuation of the above series would indicate coefficients of solubility of the order of 0·21 and 0·17, assuming the atomic weights to be 175 and 216 respectively.

The deviation from a regular series is rather to be expected in this instance, and it would be surprising if such a simple regularity were found at any particular temperature.

Furthermore, when plotting one set of values against another, *i.e.*, the values at right angles to each other, it is supposed that the quantities involved are somehow related. If the relation is one implying that the factors are interdependent, as they are regarded in the resolution of forces for example, than a resultant value (say, $\sqrt{x^2 + y^2}$) should be a truer one to study, and it should perhaps be plotted against *periodic places* when dealing with atomic weights.

Applying this principle to the boiling-points of the inactive gases—Ne, 30°; Ar, 86·9°; Kr, 121·3°; Xe, 163·9°; and RaEm about 208° (degrees C. abs.)—a straight line may be drawn through the plotted values which practically intersects all those of the group (6 elements) except the one due to helium, if the atomic weight of radium emanation is taken at 175 or about 216: the value based upon the latter figure being arranged as an *interperiodic* one. (Whether the "periodic places" should be 2^0, 2^1, 2^2, . . . &c., or logarithms of 2, 3, 4, . . . &c., instead of simply 1, 2, 3, . . . &c., is another matter possibly for consideration). Krypton is not quite on the line, otherwise the straight-line function approximately applies. Of course, helium is an exception unless it is plotted on an interperiodic line, as in the case of the other extreme member of the group. The accompanying figure shows the relations.—I am, &c.,

F. H. Loring.

February 2nd, 1911.

TURIN INTERNATIONAL EXHIBITION, 1911.

The British Section.

To the Editor of the Chemical News.

Sir,—It has been decided that in the British Section of the approaching Turin Exhibition, chemical and physical apparatus shall be shown as far as possible in a truly practical and novel manner, and I trust you will afford me, through the medium of your valuable columns, an opportunity of giving information to the public regarding the scheme.

Generally speaking, no means are provided at Exhibitions for demonstrating the utility of the instruments exhibited; and it has been felt that it would be a very great improvement to show apparatus as it would be used in a laboratory.

Accordingly, for the British Chemical Section of the Turin Exhibition, arrangements are now approaching completion by which, it is anticipated, there will be on view at least two well-equipped chemical laboratories, with such work going on as will effectively illustrate various interesting processes.

In addition there will be a large space available for the display in showcases of chemical products and apparatus not in use in the laboratories.

Smaller rooms will be provided for certain special appliances.

The Court devoted to scientific instruments will be of similar design. Here, also, arrangements are being made for the display of apparatus ready for work, electric supply, where needed, being provided.

The equipment of a large dark room is under consideration, and in this projection apparatus, such as oscillographs, spectroscopes, optical lanterns, and photometers, could be shown to advantage.

The organisation of the exhibits referred to has been placed by the Exhibitions Branch of the Board of Trade in the hands of Dr. F. Mollwo Perkin, under the direction of a joint Sub-committee of the Chemical Industries Committee and the Mathematical and Scientific Instruments Sub-committee. This joint Sub committee considers that exhibitors could not have more favourable conditions for demonstrating the merits of their exhibits than those which this new arrangement will afford, and that, at the same time, in the way of instruction by such demonstrations the visiting public will be greatly benefited.—I am, &c.,

Boverton Redwood,
Chairman, Chemical Industries Committee.

MISCELLANEOUS.

Hydrogenations in presence of Palladium.—Pierre Breteau.—In presence of spongy platinum, phenanthrene gives on hydrogenation a mixture of its tetra and octohydrides. When palladium black or precipitated palladium is used only the tetrahydride is obtained; this is the first example of hydrogenation by means of precipitated palladium.—*Comptes Rendus*, cli., No. 26.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th instant, the Duke of Northumberland, President, in the Chair. Mr. and Mrs. Alfred Carpmael, Dr. W. S. Colman, Mr. Guy Ellis, Mrs. E. B. Fielden, Dr. A. H. Levy, Mr. Basil Mott, Mr. A. F. C. Pollard, and Dr. N. Raw were elected Members. The Treasurer reported that he had received £1200, part of the legacy to the Royal Institution of the late Miss Wolfe, and £62 10s., a portion of the legacy of the late Mr. C. E. Layton. The Special Thanks of the Members were returned to Dr. J. Y. Buchanan for his Donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures. The Institution has recently received a gift of £1000 from Dr. Hugo Müller. The Special Thanks of the Members were also returned to Dr. F. Blumbach and Mr. H. N. Mladentseff for an etched portrait of the late Professor D. Mendeleeff, by the Russian artist Roondaltseff.

MEETINGS FOR THE WEEK.

Monday, 13th.—Royal Society of Arts, 8. (Cantor Lecture). "Brewing and Modern Science," by Prof. A. J. Brown.

Tuesday, 14th.—Royal Institution, 3. "Heredity," by Prof. F. W. Mott, F.R.S., &c.

Wednesday, 15th.—Royal Society of Arts, 8. "Modern Machine Bookbinding," by G. A. Stephens.

—— Microscopical, 8. "New Objectives and Eyepieces by R. Winkel, of Göttingen," by E. M. Nelson. "Recent and Fossil Foraminifera of the Shore-sands of Selsey Bill, Sussex" (Addendum), by E. Heron-Allen.

Thursday, 16th.—Royal Institution, 3. "Problems of Animals in Captivity," by P. Chalmers Mitchell, F.R.S., &c.

—— Chemical, 8.30. "Different Methods of applying the Grignard Reagents," by H. Davies and F. S. Kipping. "Formation and Reactions of Iminocompounds—Part XV., Production of Iminoderivatives of Piperidine leading to the Formation of the *ββ-dl*-Substituted Glutaric Acids," by F. B. Thole and J. F. Thorpe. "Interaction of Copper and Nitric Acid in presence of Metallic Nitrates," by F. H. Rennie and W. T. Cooke.

Friday, 17th.—Royal Institution, 9. "The Stimulation of Digestive Activity," by Prof. H. E. Armstrong, F.R.S.

Saturday, 18th.—Royal Institution, 3. "Architecture—the Byzantine and Romanesque Period," by T. G. Jackson.

THE CHEMICAL NEWS.

Vol. CIII., No. 2673.

A NEW ELEMENT ACCOMPANYING LUTECIUM AND SCANDIUM IN THE EARTHS OF GADOLINITE: CELTIUM.

By G. URBAIN.

Most of the rare earths which I have been investigating during the last few years have been obtained by a treatment of xenotime on a large scale. From the ytterbium extracted from these earths I have approximately isolated a new element—lutecium,—but I had to discontinue my purifications owing to lack of material.

I have since treated the earths of gadolinite in order to add to my supply of lutecium. By continuing the fractionation of these earths by the crystallisation of the nitrates in nitric acid of density 1·3, I obtained, after a great number of crystallisations, some drops of mother-liquor which would not crystallise.

All kinds of impurities arising either from the vessels or the reagents necessarily accumulate in the successive mother-liquors. I subjected these mother-liquors to different treatments—with sulphuretted hydrogen, ammonia, and oxalic acid—so as to eliminate anything in the substance which did not belong to the group of rare earths. I then examined the purified and perfectly white earth.

The determination of the coefficient of magnetisation of this oxide gave me the extremely low value $4{\cdot}1 \times 10^{-6}$. My best oxides of lutecium extracted from xenotime have coefficients of magnetisation which are three or four times as high.

Spectrographic analysis reveals in this substance, besides lutecium and a trace of neoytterbium, scandium and negligible traces of calcium and magnesium. There was certainly too little scandium in the earth to cause such a diminution of the paramagnetism of lutecium oxide. The lowering of the magnetism must be attributed to some other substance.

On comparing this spectrum with those of lutecium, xenotime, neoytterbium, and scandium, I found a fairly large number of lines, among which some were very strong. After having measured these lines I compared their wavelengths successively with those of the line of the arc spectra of all known substances. I was thus only able to observe accidental coincidences, which all disappeared on a more careful examination.

The principal lines of this arc spectrum between $\lambda = 2450$ and $\lambda = 3700$, the limits between which my measurements ranged, are as follows:—

2459·4	Medium	2870·2	Medium
2469·3	Medium	2885·1	Fairly strong
2481·6	Fairly strong	2903·9	Fairly strong
2536·9	Fairly strong	2931·7	Medium
2677·7	Medium	2949·5	Fairly strong
2685·2	Very strong	3080·7	Very strong
2729·1	Strong	3118 6	Very strong
2737·9	Medium	3171·4	Strong
2765·8	Very strong	3197·9	Very strong
2834·3	Fairly strong	3326·0	Fairly strong
2837·3	Fairly strong	3391·5	Strong
2845·2	Strong	3665·6	Medium

The chloride of this earth is rather more volatile than the chloride of lutecium, but less volatile than that of scandium.

Its hydroxide is a weaker base than lutecium oxide, and a stronger base than scandium oxide.

In all its other characteristics this earth shows an equal esemblance to lutecium and scandium.

As there is no doubt about the identity of this new earth, and as I have finally obtained it in a highly concentrated state, I propose to give the name celtium, symbol Ct, to the element which corresponds to it.

It is very remarkable that celtium does not occur (or at least occurs only in infinitesimal traces) in the earths of xenotime, for I have noticed the presence of the strongest of these lines in the lutecium extracted from this mineral. —*Comptes Rendus*, clii., 141.

OXIDATION IN SOIL.*

By M. X. SULLIVAN and F. R. REID.

The advantage of aërating soils has long been known, and is well recognised in the practice of tillage of the soil. Liebig early pointed out the importance of a thorough aëration of soils (Liebig's "Complete Works on Chemistry," 1852, p. 44). The phenomena of oxygen absorption by soils likewise early attracted attention. According to Liebig (*Ibid.*, p. 113), Ingenhouss and De Saussure found that vegetable mould extracted oxygen from air with great rapidity, and replaced it by an equal volume of carbonic acid. Dehérain and Demoussy (*Ann. Agron.*, 1896, xxii., 305) considerably later studied the process of oxygen absorption in several soils, and found that oxygen was always taken up and carbon dioxide set free. In their method the soils were placed in a closed tube kept at constant temperature, and after a certain time the gases were extracted, and the carbon dioxide and oxygen determined. The carbon dioxide formed was taken as a measure of oxidation. The oxidation was attributed by them to the action of micro-organisms and to simple chemical action. Both kinds of oxidation increase with heat. Up to 65° C. the carbon dioxide increased. From 65° to 90° it decreased. Above 90° there was another increase in carbon dioxide. At 110° over six times as much carbon dioxide was formed as at 65° C. Some oxidation went on at 22° C. in soils which had been heated at 120° C. for one hour. Often more oxygen was consumed than could be accounted for in carbon dioxide formed.

Wollny studied the rate of oxidation by determining the amount of carbon dioxide produced in a given time at a constant temperature ("Die Zersetung der Organ. Stoffe. und die Humusbildungen," Heidelberg, 1897). He concluded that the oxidation is due mainly to the activity of micro-organisms. Lime favoured oxidation. Chlorides and sulphates retarded, while phosphates and nitrates favoured.

More recently still Russell studied oxidation by estimating the oxygen absorbed by soils (*Journ. Agric. Sci.*, 1905, i., 261). He found that the same factors which influence fertility also influence the rate of oxidation, and apparently to the same extent, that oxidation was greater in fertile soils than in infertile soils, in surface soil than in sub-soil. With different soils of the same type the rate of oxidation varies in the same way as the fertility, and may be used to measure it. Pasture soils, however, are excluded. Russell suggests that the oxygen absorbed measures the total action of micro-organisms which, by producing enzymes, &c., hasten decomposition.

As shown by Russell, the assumption that the evolution of carbon dioxde is proportional to the amount of oxygen absorbed is not proved. Many soils, as is well known, have a great power of absorbing carbon dioxide. Russell's method of measuring the amount of oxygen absorbed is a very good method, but requires a somewhat complex apparatus, takes considerable time to show differences in soils, and marks respiration of micro-organisms as much as oxidative changes in the soil constituents. A simpler test of oxidative processes in soils we have found in the

* Contribution from the Laboratory of Soil Fertility Investigations. Published by permission of the Secretary of Agriculture. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 1.

Table I.—*Oxidation in Soils.*

Soils.	Reagents. Guaiac.	Guaiac + H_2O_2.	Aloin.	Aloin + H_2O_2.	Hydro-quinone.	Hydroquinone + H_2O_2.	Pyro-gallol.	Pyro-gallol + H_2O_2.	Paraphenylene-diamine + H_2O_2.
1. Clarksville loam ..	+	++	+	+	+ sl	++	+	++	+
2. Takoma lawn soil ..	–	–	–	–	–	–	–	?	?
3. Marshall clay loam..	–	–	–	–	–	–	–	?	–
4. Volusia silt loam ..	–	–	–	–	–	–	–	?	?
5. Arlington clay loam .	+ sl	+ sl	+ sl	+ sl	–	–	+	+	?
6. Hagerstown loam in sod	+	++	+	+	+ sl	++	+	++	+
7. Hagerstown loam ..	+	++	+	+	–	+	+	++	+
8. Hagerstown loam + lime..	+	++	+ sl	+	–	++	+ sl	++	+
9. Hagerstown loam + lime + manure ..	+	++	+ sl	+	–	++	+ sl	++	+
10. Hagerstown loam + complete fertiliser..	+	++	+	+	–	+	+	++	+
11. Hagerstown loam + manure	+	++	+	+	–	?	+	++	+
12. Norfolk fine sandy loam	–	–	–	–	–	–	–	–	–
13. Cecil fine sandy loam	–	–	–	–	–	+	+	–	?
14. Leonardtown loam ..	–	–	–	–	–	–	–	–	–
15. Dekalb silt loam ..	+	+	+	+	–	+ sl	+	+	+
16. Duchess silt loam ..	–	–	–	–	–	–	–	–	–
17. Sassafras silt loam ..	+ sl	+ sl	+ sl	+ sl	–	–	–	–	–
18. Orangeburg loam ..	+	+	+	+	–	+	+	+	+

changes produced in easily oxidisable substances brought in contact with the soil, such as aloin, pyrogallol, hydroquinone, paraphenylenediamine, benzidine, guaiac, *a*-naphthylamine, which speedily show oxidative processes, and have been used extensively as a test of such processes. By means of these easily oxidisable chromogenic substances the plant roots have been shown to have a strong oxidative power (Schreiner and Reid, *Bot. Gaz.*, 1909, xlvii., 355). This power was found to be affected by agencies which affected soil fertility, such as fertiliser salts, toxic substances, &c., and was shown to have a considerable agricultural interest in that it could affect alteration in the soil constituents, and thus influence soil fertility, especially in connection with fertilisers and a system of crop rotation. Micro-organisms which abound in soil likewise have been found capable of bringing about powerful oxidation of substances in the medium in which they grow.

The oxidising principles, be they enzymes or other bodies, were found in water in which the roots of growing seedlings had stood for twenty-four hours. Woods has reported that the oxidising enzymes may remain in soil for a considerable time (*Centralbl, f. Bakt.*, 1899, II., v., 745). So it should be expected that, by the disintegration of micro-organisms and plant roots, the material which brings about oxidation should be left in soil. In addition the soil *per se* should have, *à priori*, an oxidising power due to inorganic oxygen carriers like salts of iron and manganese, and probably to organic matter in an unstable highly oxygenated state analogous to quinone, benzaldehyde. terpene bodies, or organic peroxides, which might readily give up oxygen in an active state or activate the oxygen of the air.

In passing, it may be said that absorption of oxygen by a soil and the oxidation of readily oxidisable substances, such as the chromogens mentioned, by the soil are not necessarily the same phenomenon. In fact, the two methods might be employed together with advantage in the study of different phases of soil oxidation.

Of the reagents employed to test the oxidising power of the soil, a water solution of aloin was found to be best. The results with this and various other reagents are given in Table I.

In the experiments given in Table I., 10 grms. of soil were shaken in test-tubes with 25 cc. of 2 per cent alcoholic guaiac, 0·125 per cent water aloin, 0·5 per cent pyrogallol and hydroquinone. When hydrogen peroxide was added, it was to the extent of 0·5 cc. of a 3 per cent solution to each tube. In case of testing with paraphenylenediamine, 25 cc. of a solution of a 2 per cent solution of paraphenylenediamine plus 0·2 per cent hydrogen peroxide, containing 1 cc. of concentrated sulphuric acid to the litre, were shaken with the soil. When oxidised the reagent develops a blue-black colour. The control solution oxidised so readily, however, that it was not considered a good medium for testing oxidation, and was regarded as too sensitive for differential work.

As regards the significance of the oxidation as given in the preceding, it may be said that soils known to have good productive power had strong oxidative power, as a rule, and that the poorer soils had little or no oxidative power. The oxidative power and productivity, however, do not necessarily agree, since we have found soils of slight oxidative power which have given the better growth as compared with soils of stronger oxidising power. Crop production, as is well known, is dependent upon many factors, no one of which can be taken as an absolute criterion. As will be shown later, however, certain factors which favour productiveness of soils favour oxidation, so the study of oxidation in soil has considerable value in relation to soil fertility.

Method of Testing Oxidation in Soil.

Since aloin dissolved in water proved to be the best medium for testing oxidation, a water solution of aloin, generally of a strength of 0·125 per cent, was employed in the further study of oxidation in soil. As a rule, 20 grms. of soil were shaken four or five times in the course of an hour with 50 cc. of the aloin solution, and allowed to settle; then the mixture was treated with 50 cc. of 95 per cent alcohol to flocculate the soil and to extract the oxidised aloin. If the oxidised aloin solution was fairly clear, the alcohol was dispensed with. The solution was then centrifuged, the supernatant liquid poured off, and the depth of colour in the solution compared by means of a colorimeter. The experiments from the time of adding the aloin to the soil to the reading in the colorimeter ran, as a rule, from two to three hours.

Effect of Various Treatments on Soil Oxidation.

Poisons and Antiseptics.—Reducing agents like hydroxylamine hydrochloride, oxalic acid, sodium thiosulphate, and

formaline totally check the oxidation by soils. Mercuric chloride, silver nitrate, and carbon bisulphide had little retarding action on the oxidation, and sometimes even increased it, though of themselves these antienzymotic substances have no effect on aloin within the time of the experiment. Though the soil by its absorbing and combining powers renders toxic agents less effective than they would be in solution, the fact that oxidation goes on in the presence of comparatively strong solutions of mercuric chloride, 5 cc. of a 1 per cent solution to 20 grms. of soil, silver nitrate, 5 cc. of a 1 per cent solution to 20 grms. of soil, and carbon bisulphide, 2 cc. of a 100 per cent solution to 20 grms. of soil, would indicate, contrary to our expectation, that little, if any, of the oxidising action of the soils tested can be attributed to enzymes, though in other soils or under other conditions it may be possible that the oxidising enzymes play a considerable *rôle*.

Dry Heat.—Several soils which showed a strong oxidation toward aloin were heated one and a-half hours at 105° C. dry heat, and after cooling were shaken with the aloin solution. The oxidation of the aloin was reduced considerably by heating in the case of most of the soils tested. In some cases, especially in the Hagerstown loam, the heated soils gave such a different shade of colour with so much of the original yellow of the aloin solution, that their oxidative power could not be compared accurately with that of the normal soil. As read by means of the colorimeter, the comparative oxidation was judged to be as follows:—Clarksville loam, unheated 100, heated 100; Orangeburg loam, unheated 100, heated 111; Sassafras silt loam, unheated 100, heated no oxidation; Arlington clay loam, unheated 100 (slight), heated no oxidation; Hagerstown loam, unheated 100, heated 66; Hagerstown loam (manured), unheated 100; heated 45; Hagerstown loam plus complete fertilisers, unheated 100; heated 66.

Steam Heat.—Heating the soils for one and two hours respectively, in an Arnold steam steriliser lessened oxidation in most soils, but had no retarding effect on Orangeburg loam. The relative oxidations of the unsteamed and steamed soils are given in the following table:—

TABLE II.—*Effect of Steam Heat on the Oxidative Power of Soils.*

		Steamed.	
	Unsteamed.	1 hour.	2 hours.
Hagerstown loam	100	65	Faint
Hagerstown loam manured	100	52	Faint
Hagerstown loam plus complete fertiliser	100	34	Faint
Sassafras silt loam	100 sl	Neg.	Neg.
Arlington clay loam	100 sl	Neg.	Neg.
Clarksville silt loam	100	54	Faint
Orangeburg loam	100	104	105

Heat is a more effective inhibitor of the oxidative power of the soil than are the powerful anti-enzymotic substances such as mercuric chloride, silver nitrate, and carbon bisulphide. As compared to heat, these reagents retard oxidation but little, and in some soils silver nitrate and carbon bisulphide even increase oxidation. Accordingly, it is to be judged that the effect of heat on oxidation by soils is due to its effect on the soil ingredients, and especially on the organic matter or some inorganic-organic complexes of the soil, since steam heating for two hours would affect strictly inorganic salts destructively but little, if at all. The organic matter of the soil, however, is known to undergo considerable modification at the temperature of 100° C. (see in this connection Lyon and Bizzell, *Bull.*, 1910, cclxxv., Cornell Univ., Agr. Exp., Sta.).

Incineration.—When various soils which had a strong oxidative power toward aloin were incinerated the oxidative power was lost.

Acids on Incinerated Soils.—The addition of mineral acids such as hydrochloric and sulphuric had little effect in restoring the oxidative power of these soils. Acetic acid had a slight restoring effect. The organic hydroxy acids, on the other hand, greatly restored the oxidative power of the incinerated soils. Taking the Hagerstown loam plus acetic acid as 100, the comparative effect of the organic acids added to the incinerated soils is shown in the following table:—

TABLE III.—*Effect of Organic Acids on the Oxidative Power of Incinerated Soils.*

Soils.	Acetic.	Glycolic.	Malic.	Citric.
Hagerstown loam, manured	100	184	180	223
Hagerstown loam, complete fertiliser	100	184	180	223
Hagerstown loam	100	172	192	238

It would seem from the preceding table that the organic hydroxy acids are more effective in restoring the oxidative function of incinerated soils than are non-hydroxy acids or the mineral acids. Of the hydroxy acids tried, citric acid was the most effective in renewing the oxidative power of the incinerated soil.

Acids on Normal Soils.—In a similar way the hydroxy acids added to normal soils tended to increase the oxidative power while related non-hydroxy acids had little effect on oxidation. Thus acetic acid slightly retarded or but little increased oxidation, while the related hydroxy acid, glycolic, increased oxidation to a great degree; succinic acid had little effect on oxidation or retarded it, while the related hydroxy acids, malic and tartaric, greatly increased oxidation; citraconic, itaconic, and mesaconic acids had little effect on oxidation in soil, while the related hydroxy acid, citric, greatly increased oxidation. Of the hydroxy acids, citric is somewhat the greater activator.

In some soils sodium citrate and tartrate were greater stimulators of oxidation than were equivalent quantities of the free acids. In every case, citric acid and sodium citrate increased oxidation more than tartaric acid or sodium tartrate. Dihydroxystearic acid slightly reduced oxidation in soil, while the potassium and calcium salts slightly increased it.

(To be continued).

REPORT ON CHEMICAL CONSTITUTION AND THE ABSORPTION OF LIGHT.*

By W. W. STRONG.

(Continued from p. 65).

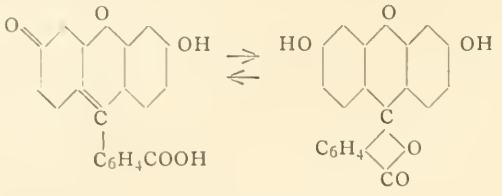
Theory of Dynamic Isomerism.

BALY, Stewart, Desch, and others have recently supported the view that the absorption of light by organic compounds does not take place under ordinary conditions, but only when there is a change in the union of the atoms. In some cases this change of union takes place when a chemical compound changes into an isomeric form. Dynamic isomerism takes place when there is some third substance to act as a sort of go-between. Many substances are isodynamic only at high temperatures or in the presence of a catalytic agent. Sometimes the solvent may promote isomeric change. The point of equilibrium is determined by the velocities of the isomeric change, and these velocities are affected by the solvent, concentration, temperature, catalytic reagent, or the presence of free alkalis or acids.

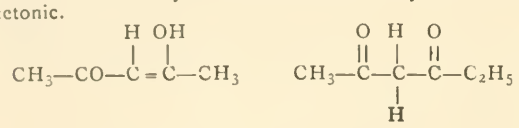
An example of the above change is the transfer of a labile hydrogen atom from an oxygen or sulphur atom to a carbon or nitrogen atom. Sometimes an OH or CN group is transferred in the same way. The atom or radical transferred assumes a neutral condition compared with its condition as a powerful negative radical in the inorganic acids.

* This Report is based upon an article by H. Ley, entitled "Ueber die Beziehung Zwischen Lichtabsorption und Chemischer Konstitution bei Organischen Verbindungen." See *Jahrbuch der Radioaktivität und Elektronik* 1910, vi., 274. From the *American Chemical Journal*, xliv., No. 1

The theory of dynamic isomerism is useful in explaining a large number of phenomena in organic chemistry, and especially those connected with light emission and absorption. Tschugaeff (*Ber.*, 1901, xxxiv., 1820) has examined some five hundred compounds for triboluminescence (luminiscence due to the crushing of the compound), and has found that 25 per cent of the organic compounds investigated showed a more or less intense flash when crushed. Most of the luminescent compounds could have existed in several isodynamic forms. Phosphorescence and fluorescence may be explained as being due to a dynamic isomerism existing between two or more forms. For instance, fluorescein may exist in two or more forms:—

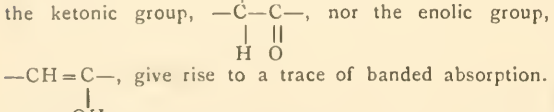


We shall now consider some recent work by Baly and Desch. They first took up acetylacetone, $CH_3\ CO{-}CH_2{-}CO{-}CH_3$, and ethyl acetacetate, $CH_3{-}CO{-}CH_2{-}CO_2C_2H_5$, and their metallic derivatives. Acetylacetone and its metal derivatives were found to give similar spectra. Ethyl acetacetate was found to give only a very slight general absorption, whereas its aluminium derivative gave a spectrum almost exactly like that of acetylacetone. Now the work of Perkin and others has shown that free acetylacetone is enolic and ethyl acetacetate ketonic.

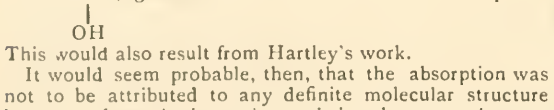


Acetylacetone (enolic). Ethylacetacetone (ketonic).

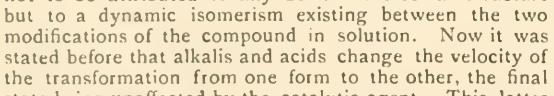
These results would then indicate that the metallic derivatives of ethyl acetacetate have the enolic structure, the metal taking the place of hydrogen in the OH group. But by using various compounds it was shown that neither



the ketonic group, —C—C—, nor the enolic group,



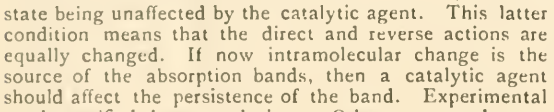
—CH=C—, give rise to a trace of banded absorption.



This would also result from Hartley's work.

It would seem probable, then, that the absorption was not to be attributed to any definite molecular structure but to a dynamic isomerism existing between the two modifications of the compound in solution. Now it was stated before that alkalis and acids change the velocity of the transformation from one form to the other, the final state being unaffected by the catalytic agent. This latter condition means that the direct and reverse actions are equally changed. If now intramolecular change is the source of the absorption bands, then a catalytic agent should affect the persistence of the band. Experimental results verified these conclusions. Other compounds were tried with similar results.

From these results it follows that there must exist, in connection with the reversible transformation of one tautomeric form into the other, a system which is synchronous with the light absorbed. This cannot be a vibration of the labile atom itself, for the oscillation frequency of the absorption bands does not bear any direct relation to the mass of the labile atom, and the frequency of atomic motions is never so high as these. The absorption must be due, however, to the oscillation of linking of the keto-enol tautomers:



where the asterisks indicate the points where the migrations of linkages occur. From a summary of work previously done on ultra-violet absorption spectra, it was seen that most of the compounds showing absorption also were tautomeric. As was also seen, an increase of the mass of the molecule in general decreased the oscillation frequency of the absorbed light, although by only a small amount.

Assuming the saturnian form of atom similar to the arrangement assumed by J. J. Thomson, chemical bonds would simply consist of Faraday tubes of force. Now, by a re-arrangement of Faraday tubes, it is quite probable that a vibrational disturbance would be set up. If Hewitt's explanation of the origin of fluorescence is correct, it would follow that disturbances set up by isodynamic changes are of the same frequency as light waves. The luminosity due to thermal or electric action is caused by rapid changes of stress or of the electric action to which the atoms are subjected. Here the disturbances of the electrons are due to the oscillation of linkages within the molecule. The comparatively small displacement of the absorption band by a change in the mass of the molecule is to be expected, for an increase of the mass of matter near a vibrating electron has the effect of retarding its motion, the oscillation frequency becoming less. For instance, the spectral series of Kayser for various related elements show a displacement towards the red on increasing the atomic mass. This is in general true for all emission spectra and for the absorption spectra of the rare earths and organic dyes.

The sodium and aluminium derivatives of ethyl acetacetate show the enolic and ketonic modifications in dynamical equilibrium. The sodium compound is found to be easily decomposed into sodium hydroxide and ethyl acetacetate, whereas the aluminium derivative shows dissociation and hydrolysis to but a very small extent. The absorption spectrum is not dependent on ionisation or hydrolysis. Hartley has found that the ultra-violet absorption spectra of metallic nitrates is exhibited even on very great dilution, showing a close connection between the anion and cation in such solutions. Baly and Desch conclude that the Faraday tubes may be lengthened out on dilution, and that the force necessary for the separation is furnished by the attraction of the solvent. Solvents which thus exert a strong attracting force are ionising agents; and this attraction is exerted both on molecules and ions. We have thus hydrated molecules and ions. When the Faraday tubes are lengthened beyond a certain critical value, an interchange of ions between the molecules becomes possible. A completely dissociated solution of a salt is not one in which the ions are moving independently of one another, but one in which the length of the Faraday tubes is greater than the critical value. In tautomeric compounds the Faraday tubes connect the labile atom with the rest of the molecule, being lengthened out to such an extent as to allow these atoms to change their positions in the molecule, and there is a sort of internal ionisation within the molecule. To this making and breaking of Faraday tubes may be attributed the absorption of the light.

In the tautomeric aliphatic compounds the substitution of an alkyl group for the labile atom destroys the tautomerism. This would be expected, for alkyl ions are unknown. Water and other solvents do not have sufficient attractive force to lengthen out the Faraday tubes in this case. Whether there is a banded absorption in these cases is not stated. One consequence of the theory can be tested. Since the persistence of the absorption band is a measure of the number of molecules undergoing transformation at any moment, this persistence should reach a limit for each tautomeric compound when the length of the Faraday

tubes has reached their critical length, so that free interchange takes place. By the successive addition of an accelerating compound a maximum should be found. Experiment shows this to be true. Take the case of ethyl benzoylsuccinate, to which 1, 10, 20, and 100 equivalents of sodium hydroxide have been added. The limits of persistence referred to a 0·0001 normal solution of the ester are as follows :—

	Free ester.	1 eq. NaOH.	10 eq. NaOH.	20 eq. NaOH.	100 eq. NaOH.
Absorption band begins at (mm.)	120·0	63·0	40	31·7	21·9
Absorption band ends at (mm.)	83·2	34·7	20	15·2	10·4
Change of dilution over which the band persists (per cent)	30·7	44·9	50	52·0	52·5

At this point it may be well to refer to the work of Stewart and Baly. Quite a number of chemical facts have been explained by the theory of steric hindrance, although this theory also fails to explain a great many things. For instance, acetic acid, CH_3COOH, is esterified with ease. The methyl, ethyl, &c., derivatives are much more difficult to esterify. This is explained as due to the larger volumes occupied by these radicals, and the consequent hindrance to the approach of the alcohol to the carboxyl radical. If, as is probable, however, the intramolecular mean free path is large compared to the size of these radicals, this explanation by steric hindrance breaks down. The theory of isodynamic change will explain all these facts and also others where the theory of steric hindrance would lead to conclusions directly contrary to the facts. According to this theory acetacetic ester exists as—

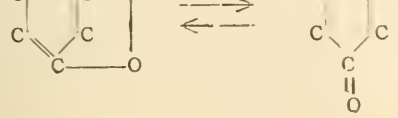
$$CH_3{-}C(OH)=CH{-}COOC_2H_5 \rightleftharpoons CH_3{-}C(=O){-}CH_2{-}COOC_2H_5.$$

During this dynamic equilibrium there are periods during which a nascent carbonyl group exists. From analogy to the action of other nascent substances, this would occasion a very much greater reactivity.

Stewart and Baly, on further investigation, found that the absorption band in this case has a persistence which decreases proportionately to the decrease of reactivity of the ketone's carbonyl group. It has been noticed by chemists that the velocity of tautomeric change depends on the solvent. Stewart and Baly also found that the persistence of the absorption band was very different in aqueous and alcoholic solutions. In the case of pyruvic ester they show that the facts may be represented by the scheme—

$$CH_3{-}C(=O){-}C(=O){-}OC_2H_5 \rightleftharpoons CH_3{-}C(=O){-}C(-O){=}OC_2H_5.$$

In tautomerism we have a wandering of the hydrogen atom, so Stewart and Baly propose to call this process Isorropesis (from the Greek word *ἰσορροπεία*, equipoise), or an oscillation in the carbonyl grouping. By the persistence of absorption bands it is possible to measure the activity of chemical compounds. The band produced by the isorropesis is also much nearer the red than that produced by the process of enol-keto tautomerism. An example of isorropesis would be the quinone band 1/λ—2480, which would be due to the following change :—



In general, then, according to the theory of Baly, Desch, Stewart, and Collie, any absorption by organic compounds is due to the conditions that occur during isomeric changes. Benzene, for example, appears in two forms, and the absorption spectrum is due to a condition of benzene while it is changing from one form to the other. This theory explains quite well the action of chromophores, for, as we have seen, every chromophore contains at least one double bond.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 2nd, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows :—

"*Experiments to Investigate the Infectivity of* Glossina palpalis *Fed on Sleeping Sickness Patients under Treatment.*" By Col. Sir D. Bruce, F.R.S., Captains A. E. Hamerton and H. R. Bateman, and Dr. R. Van Someren.

"*Experiments to Ascertain if* Trypanosoma gambiense *during its Development within* Glossina palpalis *is Infective.*" By Col. Sir D. Bruce, F.R.S., and Captains A. E. Hamerton, H. R. Bateman, and F. P. Mackie.

"*Further Experimental Researches on the Etiology of Endemic Goitre.*" By Captain R. McCarrison, I.M.S.

"*Leaves of Calamites* (*Calamocladus Section*)." By H. Hamshaw Thomas, M.A., Curator of the Botanical Museum, Cambridge.

"*Complement Deviation in Mouse Carcinoma.*" By J. O. Wakelin Barratt, M.D.

The object of the present investigation is to ascertain if in mouse carcinoma antibodies are produced in respect of the tumour. The method followed is an application of the complement deviation test, an extract of mouse tumour being employed as antigen. The experiments made fall into two groups. In one the serum of the rabbit or of man was employed as the source of complement; in the other the serum of the mouse served as the source of complement. In both cases the same result was obtained—namely, that the complement deviating power of the serum of mice with tumours was sometimes greater than that of normal mouse serum, but not unfrequently the serum of a mouse with a tumour was found to be identical in respect of its complement deviating power with that of a normal mouse.

CHEMICAL SOCIETY.

Ordinary Meeting, February 2nd, 1911.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Eric Collington, Claremont, Noel Road, Edgbaston; Clement Arthur Crook, 4, Dry Clough Lane, Halifax; William Henry Dickinson, Capt. (I.M.S.), M.B., Ch.B., Grant Medical College, Bombay; Ralph Roscoe Enfield, B.A., Toynbee Hall, Commercial Street, E.; Oswald Mansell-Moullin, B.A., 69, Wimpole Street, W.; George Arncliffe Percival, 34, Cartwright Gardens, W.C.; Albert Cherbury David Rivett, B.A., B.Sc., Chemistry Dept., University, Melbourne; William Arthur Reginald Wilks, M.A., 50, Stowheath Lane, Priestfield, Wolverhampton.

Of the following papers, those marked * were read :—

*26. "*The Constancy of Water of Crystallisation in Hydrated Salts.*" (Part II.). By Herbert Brereton Baker and George Henry Joseph Adlam.

The authors have found that telluric acid always contains an excess of water over the calculated amount even when dried by phosphoric oxide for six months in a vacuum. This excess is due to water occluded in the crystals, and water vapour cannot pass through a thin crystal of this substance. Determinations of the atomic weight of tellurium have been made by estimating the weight of water given off in the decomposition of telluric acid, as well as the total loss of weight. The mean of four determinations of the ratio $TeO_2 : O$ gave an atomic weight of 127·49. Experiments have been made with other hydrated crystals to find if such substances can be obtained in such a state as to be available for atomic weight determinations. By keeping the salts in an atmosphere containing a quantity of the partly dehydrated salt, such salts can be completely freed from adherent moisture. One such experiment with crystallised barium chloride ($BaCl_2,2H_2O$) gave 14·772 per cent of water instead of 14·747. The similar method used by Guye and Tsakalotos (*Journ. Chim. Phys.*, 1909, viii., 3) gave with the same salt 14·6765 per cent of water. It was shown that if a salt be completely dehydrated and left in a moist atmosphere, it will take up almost exactly the amount of water which corresponds with its water of crystallisation. For barium chloride the percentage was 14·750 instead of 14·747.

Further, it has been shown that air will not pass through a crystal when the latter is used to close a vacuum tube. Water vapour will, however, pass through hydrated crystals from a moist atmosphere to a dehydrating agent, but a partial dehydration of the crystal on the side nearest to the dehydrating agent seems to be necessary. Water vapour will not pass through anhydrous crystals, and therefore occluded water cannot be removed by placing in a desiccating atmosphere.

Discussion.

The President asked whether it was possible to obtain anhydrous telluric acid, H_2TeO_4, and whether the ortho-acid, H_6TeO_6, could be made by allowing the more or less anhydrous acid to take up moisture from an unsaturated atmosphere.

Dr. Senter said that if he understood the author rightly it was claimed that drying a salt hydrate over a mixture of the same hydrate and the anhydrous salt would remove all the moisture from the surface of the hydrate crystals. The method in question would ensure against dehydration being carried too far, but it appeared open to doubt whether it could be relied on to effect the complete removal of adsorbed moisture in all cases when one remembered the remarkable tenacity with which such moisture was sometimes held. The data given by the authors showed that the method was effective for barium chloride, but other salt hydrates in crystalline form might conceivably have much greater power of retaining adsorbed moisture. He wished to ask Dr. Baker if further data were available on this point.

Dr. R. Lessing asked if the size of crystals had any influence on the amount of "adherent" or "occluded" water, and whether it was possible to facilitate the removal of this water by finely grinding the crystals.

In reply to the President, Dr. Baker said that anhydrous telluric acid took up water with extreme slowness. It was insoluble in water, and it did not become completely hydrated by remaining in water for three months. In answer to Dr. Senter, it was stated that the experiments now in progress would decide whether the method was a general one.

*27. "*The Triazo-group.* Part XVI. *Interaction of Nitrosates and Sodium Azide.*" By Martin Onslow Forster and Frederik Marinus van Gelderen.

The azoimide nucleus may be substituted for the nitroxyl group in nitrosates and ethereal nitrates.

β-Triazo-β-methylbutan-γ-oxime, $N_3{\cdot}CMe_2{\cdot}CMe{:}NOH$, prepared from *iso*amylene nitrosate and sodium azide, melts at 34—35°; it is freely soluble in organic media, and is volatile in steam. *β-Triazo-β-methylbutan-γ-one*, $N_3{\cdot}CMe_2{\cdot}CO{\cdot}CH_3$, produced on hydrolysing the oxime with dilute mineral acids, boils at 42°/14 mm., and has D 1·0057/18°. The *semicarbazone*, $C_6H_{12}ON_6$, and *thiosemicarbazone*, $C_6H_{12}SN_6$, melt at 127° and 106—107° respectively.

The triazo-ketone leads to the amino-ketone on reduction, but this is stable only in the form of salts; alkalis convert these into hexamethyldihydropyrazine, which has been lately described by Gabriel (*Ber.*, 1911, xliv., 57).

*28. "*The Triazo-group.* Part XVII. *Nitroso-azides of Pinene and Terpineol.*" By Martin Onslow Forster and Sidney Herbert Newman.

Nitroso-azides may be prepared by interaction of nitroso-chlorides and sodium azide. *Pinene nitrosoazide*, $C_{10}H_{15}(:NOH){\cdot}N_3$, crystallises in brilliant transparent prisms, melting at 120°; it is unimolecular, and the *acetyl* derivative melts at 64°. Alcoholic piperidine or sodium ethoxide gives rise to nitrosopinene. An *isomeride* of pinene nitrosoazide arises when the original material is heated with water, and melts at 126°; the *acetyl* derivative melting at 71°; it also yields nitrosopinene with alcoholic sodium ethoxide, but the continued action of hot water leads to the oxime of hydroxydihydrocarvone, melting at 133·5°. The last-named substance is produced also by the action of alcoholic sodium ethoxide on *terpineol nitrosoazide*, $OH{\cdot}C_{10}H_{16}(:NOH){\cdot}N_3$, which is prepared from terpineol nitrosochloride and sodium azide, and melts at 111°.

*29. "*The Synthesis of 3-β-Aminoethylindole.*" By Arthur James Ewins.

The condensation of γ-aminobutyrylacetal and phenylhydrazine, by heating with zinc chloride to 180°, yields *3-β-aminoethylindole* (m. p. 146°), the amine derived from tryptophan by loss of carbon dioxide. Its most characteristic salt is the *picrate*, red needles, m. p. 242—243°.

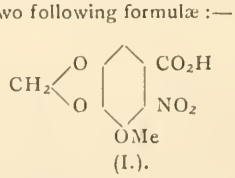
The *hydrochloride*, *picrolonate*, and *benzoyl* derivative were also described. The base is physiologically active.

Discussion.

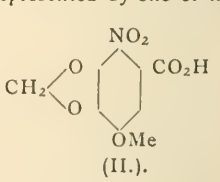
In reply to Dr. Pyman, Mr. Ewins stated that the yield of 3-β-aminoethylindole was from 40 to 50 per cent of the theoretical.

30. "*The Orientation of the Nitro-group in Nitromyristicinic Acid.*" By Arthur Henry Salway.

In a previous investigation (*Trans.*, 1909, xcv., 1155) the author had occasion to prepare nitromyristicinic acid, the constitution of which could be represented by one of the two following formulæ :—



(I.).



(II.).

It has now been shown that this acid may be converted into cotarnic acid by the transformation of the nitro-group into a carboxylic group. The constitution of nitromyristicinic acid must therefore be representated by Formula I.

31. "*The Condensation of Aromatic Aldehydes with Nitromethane.*" By Frederic George Percy Remfry.

The facility with which aromatic aldehydes condense with nitromethane in the presence of alcoholic potash is affected by the nature and position, with regard to the aldehyde radicle, of any substituting groups in the benzene ring. An attempt was made to ascertain the conditions which govern the condensation, and for this purpose a number of aldehydes, with different substituents variously placed in the ring, were condensed with nitromethane.

The results obtained, however, did not permit of any generalisation being put forward, owing to the fact that anomalies were observed in some cases which at present have not been satisfactorily explained.

The following compounds were described:—*ω-Nitro*-o-, -m-, and -p-*hydroxystyrene*, $OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}NO_2$ (m. p. 133—134°, 132—133°, and 165° respectively); *ω-nitro*-p-*acetoxystyrene* (m. p. 158—159°); *ω-nitro*-p-*benzoyloxystyrene* (m. p. 156°); *ethyl ω-nitrostyryl*-p-*oxyacetate*, $NO_2{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2Et$ (m. p. 82°); *ethyl ω-nitrostyryl*-m-*oxyacetate* (m. p. 147—148°); p-*chloro*-*ω-nitrostyrene* (m. p. 111—112°); *ω*-3-*dinitro*-2-*hydroxystyrene* (m. p. 174—175°); *ω*-3-*dinitro*-4-*methoxystyrene* (m. p. 165—166°); *α*-3:5-*trinitro*-4-*methoxy*-α-*phenylethanol*, $OMe{\cdot}C_6H_2(NO_2)_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$; *β-nitro*-2:5-*dihydroxyphenylethanol* (m. p. 182°); *ethyl* 3-*aldehydosalicylate*, $CHO{\cdot}C_6H_3(OH){\cdot}CO_2Et$ (m. p. 66—67°); *ethyl* 5-*aldehydosalicylate* (m. p. 69°), and its 3-*nitro*-derivative (m. p. 79—80°); *ω-nitro*-2-*hydroxy*-3-*carboxystyrene* (m. p. 231°); 3-*nitro*-5-*aldehydosalicylic acid* (m. p. 177°); 5-*nitro*-3-*aldehydosalicylic acid* (m. p. 195—196°), and 1-*ω-nitrovinyl*-2-*naphthol* (m. p. 187—188°).

32. "*The Phosphoric Acids.*" By Alfred Holt and James Eckersley Myers.

The experiments carried out by the authors lead to the following conclusions:—

1. Pyrophosphoric acid is formed as an intermediate compound during the hydration of metaphosphoric acid.

2. The rate of hydration does not accord with any simple order of reaction.

3. Meta- and pyro-phosphoric acids, when prepared by dehydrating the ortho-acid, give complex molecules in solution, but when prepared by decomposing the corresponding lead salts, simpler molecules result.

33. "*The Determination of Solubility Coefficients by Aspiration.*" By William Jacob Jones.

If a volume V cc. of air be bubbled through a volume *v* cc. of a well-stirred solution containing initially *a* grms. of gaseous solute, and if the air in its passage through the solution abstract and carry along with it *c* grms. of solute, then the solubility coefficient *s* of that gas in the liquid is given by the expression:—

$$s = \frac{V}{v \log_e \frac{a}{(a - c)}}.$$

A form of apparatus has been devised whereby an accurate knowledge of the quantities V, *v*, *a*, and *c*, and consequently of *s*, is rendered possible.

34. "*α-Amino-α-phenylacetamide and some of its Derivatives.*" By Charles Hugh Clarke and Francis Francis.

α-Amino-α-phenylacetamide, $C_6H_5{\cdot}CH(NH_2){\cdot}CO{\cdot}NH_2$, is easily obtained, in the form of its *benzylidene* derivative, by the action of potassium hydroxide solution and ammonia on benzaldehydecyanohydrin in the presence of benzaldehyde. From this condensation product the free base itself is isolated by the action of phenylhydrazine with subsequent separation, based on the solubility of α-amino-α-phenylacetamide in water.

α-Amino-α-phenylacetamide is a strong base, and easily condenses with aldehydes. Its *carbethoxy*-derivative lends itself so readily to the formation of hydantoin that this constitutes the best method for the formation of substances of this class. On the other hand, no derivatives of the base could be prepared from which it was possible to isolate six-membered cyclic substances.

35. "*Methylammonium Nitrite.*" By Prafulla Chandra Ray and Jitendra Nath Rakshit.

Methylammonium nitrite, $CH_3{\cdot}NH_3{\cdot}NO_2$, is formed in the interaction of mercuric nitrite and methylamine, and it is readily prepared by triturating methylamine hydrochloride with silver nitrite in the presence of a little water. On evaporating in a vacuum the filtrate after removal of silver chloride, lustrous crystals are obtained.

Methyammonium nitrate has a pale greenish yellow colour, and is extremely deliquescent. It decomposes when kept in a desiccator, and when heated, methyl alcohol and nitrogen are produced together with some secondary products of decomposition.

36. "*The Picraminobenzoic Acids and their Salts.*" By James Codrington Crocker and Frank Matthews.

The three picraminobenzoic acids and the salts derived from them were described. The ordinary salts are generally of the "acid" type, containing two equivalents of the acid radicle to one of the base. The "semi" or acid salts have the general formula $CO_2M{\cdot}C_6H_4{\cdot}NHR, CO_2H{\cdot}C_6H_4{\cdot}NHR$ (where R denotes the picramyl group). This type of salt is only moderately soluble in water, and in most cases is completely hydrolysed even in the cold by excess of water, with precipitation of the acid, alkali remaining in solution. The "normal" salts are easily soluble in water, and show little hydrolysis in solution. The following substances were prepared:—

o-*Picraminobenzoic acid* (m. p. 270°) and the acid o-*picraminobenzoates* of sodium, potassium, ammonium, methylamine, ethylamine, aniline, and pyridine; also the normal *silver* salt of *o*-picraminobenzoic acid.

m-*Picraminobenzoic acid* (m. p. 234°) and the acid m-*picraminobenzoates* of sodium, potassium, methylamine (two salts), ethylamine, and guanidine; also the normal *potassium* salt of *m*-picraminobenzoic acid.

p-*Picraminobenzoic acid* (m. p. 285°) and the acid p-*picraminobenzoates* of potassium and methylamine, and the normal salts of sodium and ammonium.

Quantitative experiments on the hydrolysis by water of the acid potassium salt of the *o*-acid were also carried out. It was shown that when the salt was in excess, equilibrium was attained when a certain constant concentration of alkali in solution was reached (about N/250 at 25°).

37. "*New Derivatives of* d-*Glucosamine.*" By James Colquhoun Irvine, David McNicoll, and Alexander Hynd.

Glucosamine hydrochloride reacts with acetyl bromide to give *bromotriacetylglucosamine hydrobromide* (m. p. 149—150°, $[\alpha]_D + 148{\cdot}4°$), which serves as the starting-point in the preparation of a number of glucosamine derivatives. The compound exists in α- and β-forms, shows normal mutarotation when dissolved in anhydrous acetone, and condenses readily with hydroxy-compounds. When acted on by traces of water, it is completely converted into glucosamine hydrobromide, owing to hydrolysis and the slow removal of the acetyl groups. By condensation with methyl alcohol, in the presence of pyridine, it gives *triacetylmethylglucosamine hydrobromide* (m. p. 230—233°), which has $[\alpha]_D + 20{\cdot}2°$ in methyl-alcoholic solution, and behaves as a β-glucoside. The acetyl groups may be eliminated from this compound by boiling with barium hydroxide, or by the action of dilute alcoholic hydrogen bromide in the cold, the reaction giving *methylglucosamine* as a strongly alkaline glucosidic syrup.

The *hydrochloride* of the latter appears to be a mixture of α- and β-stereoisomeric forms (m. p. 185—187°, $[\alpha]_D$ in water $-19{\cdot}5°$); the compound closely resembles the aminomethylglucoside hydrochloride recently obtained by Fischer (*Ber.*, 1911, xliv., 132), and is possibly identical with it. The substance is, however, remarkably stable towards hydrolytic agents, but is converted into glucosamine hydrochloride by the action of concentrated hydrochloric acid. By similar treatment, all the compounds described give glucosamine salts, and are thus true derivatives of glucosamine. The conclusion is also drawn that the use of pyridine and silver salts in the preparation of the compounds has no effect on the configuration or on the amino-group.

The work is being continued with the object of correlating glucosamine with glucose, and of preparing sugar complexes containing the glucosamine residue.

38. "*The Interaction of Silver Nitrate and Potassium Persulphate and its Catalytic Effect in the Oxidation of Organic Substances.*" By PERCY CORLETT AUSTIN.

A detailed analysis of the black precipitate, which results from the interaction of aqueous solutions of silver nitrate and potassium persulphate, was found to verify the assumption made by Marshall (*Proc. Roy. Soc. Edin.*, 1900, xxiii., 163) that the silver persulphate, first formed, is partly decomposed by water according to the equation $Ag_2S_2O_8 + 2H_2O = Ag_2O_2 + 2H_2SO_4$. The precipitate appears to be a mixture of silver dioxide, silver persulphate, and a small percentage of water in proportions which vary slightly according to the conditions of the experiment. The catalytic effect of adding a trace of silver nitrate in the oxidation of various organic substances by means of aqueous potassium persulphate was studied. Whereas, in the absence of silver nitrate, oxidation did not appear to take place, the presence of a trace of this catalyst produced a very marked effect with toluene, when benzaldehyde and benzoic acid were quickly formed. Under similar conditions, thymol gave dithymol.

39. "*The Isomerism of Ferrocyanides.*" By SAMUEL HENRY CLIFFORD BRIGGS.

The author finds that ferrocyanides exist in two forms, which are related to each other in the same way as are the α- and β-ferricyanides of Locke and Edwards (*Am. Chem. Journ.*, 1899, xxi., 193, 413), and which have therefore been termed α- and β-ferrocyanides. The α-ferrocyanides of the alkali metals are lemon-yellow in colour, and the β-ferrocyanides are orange- or amber-coloured. The difference in colour persists in solution, and when one form is converted into the other in solution, a corresponding change in colour is observed.

Acids convert the α-ferrocyanides into β-ferrocyanides; cyanides, ammonia, and alkalis effect the opposite transformation.

Nine ferrocyanides have been obtained in the two modifications. The α- and β-ferrocyanides of *l*-methylammonium have $[\alpha]_D$ 17 $-42°$ and $-28°$ respectively in absolute alcoholic solution. The conversion of the α-ferrocyanide into the β-ferrocyanide is accompanied by a corresponding fall in specific rotation.

The α- and β-ferrocyanides are related to each other in the same way as the green and yellow platinocyanides of Levy (*Trans.*, 1908, xciii., 1446).

Reasons were adduced to show that the α- and β-ferrocyanides are stereoisomeric in accordance with the author's theory of complex salts (*Trans.*, 1908, xciii., 1564).

PHYSICAL SOCIETY.

Ordinary Meeting, January 27th, 1911.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

"*A Demonstration of the Phase Difference between the Primary and the Secondary Currents of a Transformer by means of Simple Apparatus,*" was given by Prof. F. T. TROUTON, F.R.S.

The apparatus is a primitive induction motor consisting of two horseshoe electromagnets with their axes coincident and vertical, and their planes at right angles. Above the poles a copper disc is pivoted. The primary current from a transformer is sent through one magnet and the secondary current through the other. With a suitable phase difference a rotating magnetic field is thus obtained. The phase difference between the currents is—

$$\phi = \frac{\pi}{2} + \tan \frac{-1Lp}{R},$$

L and P being the inductance and resistance of the secondary circuit. By increasing L, ϕ tends to π, and consequently the torque acting on the disc becomes small. Increasing R makes ϕ tend to $\pi/2$, and a larger rotation is obtained. Inserting an iron core into the transformer diminishes the speed of rotation owing to the increase of L and also to the fact that the hysteresis in the iron causes the secondary circuit to lag still more behind the primary. Lags greater than π may be obtained when the rotation is in the opposite direction, and may be reduced to nothing by increasing the resistance. A steel core will produce a greater negative rotation than an iron one. To demonstrate the hysteresis effect it is necessary that the core should consist of a bundle of fine wires, otherwise the Foucault currents set up will introduce a lag. The effect of Foucault currents can be shown by introducing another coil within the transformer in place of the iron core and closing its circuit with a variable resistance when lags $>$ or $<\pi$ may be obtained according to the resistance.

The hysteresis is greatly modified by subjecting the core to a permanent magnetic field by means of an additiona coil on the transformer. Moderate fields increase the hysteresis, though large fields decrease it. This is due to working on the knee of the hysteresis curve in the first case, while in the second case the core is permanently saturated, and acts as a non-magnetic substance.

Dr. W. E. SUMPNER pointed out that introducing an iron core produced several effects; for instance, the magnitudes of the currents were altered as well as the sel and mutual inductions.

Prof. S. P. THOMPSON said that Mr. Baily showed a similar apparatus at the Physical Society thirty years ago.

Prof. G. W. O. HOWE pointed out that Foucault currents would be induced in the closed coil used for magnetising the iron core.

Mr. A. CAMPBELL called attention to an instrument by means of which Lissajou figures were obtained from the combined oscillations of the primary and secondary currents.

The AUTHOR, in reply to Prof. HOWE, stated that a coil with a high resistance was employed for magnetising the core, to avoid the effect he mentioned.

A Paper entitled, "*A Note on the Experimental Measurement of the High-frequency Resistance of Wires,*" was read by Prof. J. A. FLEMING, F.R.S.

The author refers to a paper read by him in December, 1909, before the Institution of Electrical Engineers on "Quantitative Measurements in Connection with Radiotelegraphy" (*Journ. Inst. Elect. Eng.*, 1910, xliv., 349), in which he described an apparatus consisting of a differential air thermometer having tubular bulbs into which similar wires could be placed, and by means of which a comparison could be made of the high frequency (H.F.) resistance R′ of a straight wire and its steady or ohmic resistance R. If two equal wires have passed through one, a steady current A and through the other a H.F. current A_1, then if these currents are adjusted until the rate of heat evolution in each case is the same, we have $A^2R = A_1^2R'$. Certain precautions are described in the paper for eliminating inequalities, but by means of correct reading H.F. ammeters as devised by the author, the ratio of the resistances R′/R can be determined from the ratio of the mean square currents A^2/A_1^2.

The H.F. currents used were obtained by condenser discharges and the equiheating steady current determined by means of the differential thermometer arrangement having two equal wires in the two tubular bulbs. It is then shown that the results for straight wires agree very well with the formulæ given by Lord Kelvin and by Dr. A. Russell for the ratio R′/R for wires of different sizes and for different frequency. It is pointed out that the correction to be applied for damped oscillations, as compared with persistent oscillations is at most 1 per cent in the cases measured, and that the correction for the heating effect of the condenser charging current is negligible. The case o spiral wires is then discussed. The resistance R″ of a spiral is greater than that of the same wire R′ stretched out straight. In the cases examined the ratio R″/R exceeds R′/R by about 50 to 80 per cent. A formula given by Dr. Nicholson for R″/R is then discussed, and

is shown that it does not agree with the results of observation. Experiments are also described on the H.F. resistance of wires of magnetic metals, and it is shown that in this case the observed value of R'/R can be used to determine the permeability for small H.F. magnetising forces.

Dr. A. Russell pointed out that in obtaining the formula for the high-frequency resistance of iron wires it is not justifiable to assume μ to be constant.

Mr. Duddell remarked that he had made some experiments with insulated wires, and had found that this increased the resistance, possibly owing to condenser action.

Dr. Erskine-Murray said the instrument would certainly be useful to those interested in wireless telegraphy.

Major O'Meara thought the method was well worth following up.

Prof. E. Wilson drew attention to the inductive action between the two circuits, which might not be negligible in the case of a spiral.

A paper on the "*Measurements of Energy Losses in Condensers Traversed by High Frequency Electric Oscillations*," by Prof. J. A. Fleming and Mr. G. B. Dyke, was read by Prof. Fleming.

In this paper an arrangement of apparatus is described for the purpose of measuring the internal energy losses in condensers traversed by high-frequency (H.F.) currents. It is shown that these energy losses in condensers may be considered as if they were due to a resistance loss in a hypothetical resistance in series with the condenser, the condenser itself being supposed to have a perfect non-dissipative dielectric of the same dielectric constant. This hypothetical resistance is not constant, but is a function of she condenser current. The experiments were conducted by the use of a special form of impact dischargers comprising two flat plates immersed in oil, one stationary and the other revolving at a high speed. This discharger was placed in series with a primary circuit and condenser, and H.F. oscillations were set up in the primary having any desired frequency. A secondary circuit loosely coupled consisted of a wire whose H.F. resistance could be determined, the condenser to be examined and a hot-wire ammeter and variable resistances. The measurements consisted in observing the reading of the ammeter, and then changing the current created in the secondary circuit by a small amount by adding a known resistance which altered the decrement of the circuit, but not its inductance. From these readings an equation is obtained for the hypothetical condenser resistance. It is shown that the product of the square of the secondary current A^2 and the total resistance R of the secondary circuit is constant, and hence that the unknown condenser resistance ρ can be found from observations of the change in A^2 when an additional resistance r_1 is interpolated in the condenser circuit. The energy loss in the condenser is then $A^2\rho$ watts. Condensers with various dielectrics, air, oil, glass, and ebonite, were examined, and the dielectric energy losses D are stated in micro watts per cubic centimetre of dielectric for given values of the electric force E. It is shown thus D can be expressed as a function of E in the form $D = XE^Y$, where X is a constant depending on the current density, and Y is a constant depending on the nature of the dielectric. For oil and air these power losses are relatively small, but for glass and ebonite large. The necessity for measuring these losses in the case of radio-telegraphic condensers is emphasised.

A paper on "*Some Resonance Curves taken with Impact and Spark Ball Dischargers*," by Prof. J. A. Fleming and Mr. G. B. Dyke, was read by Prof. Fleming.

In the course of the experiments described in the previous paper on the measurement of energy losses in condensers a large number of measurements had to be made with the cymometer of the frequency of oscillations in, and the inductance of, the secondary or condenser circuit. It was then an easy matter to draw complete resonance curves in each case, and this has accordingly been done with both the impact and spark ball dischargers in the primary circuit and for various resistances in the secondary circuit. The results are interesting as showing exactly what takes place in each case in the primary circuit. If we are using the spark ball discharger, and if the primary and secondary circuits are coupled with various degrees of coupling, then, for any close coupling, we find on the resonance curve three peaks which correspond respectively, as regards frequency, with the free oscillation period of the secondary and with the two-period oscillations set up by the reaction of the secondary upon the primary circuit. As the coupling is weakened the double-period oscillations die out, and only the free oscillation of the secondary survives. There is always a certain coupling, not far from 10 per cent, which gives the maximum current in the secondary circuit in the form of a free oscillation. If the secondary circuit is more highly damped, then the two period oscillations are more strongly marked, and the maximum free period oscillation has a lesser maximum value.

If we are using an impact discharger the double-period oscillations are only apparent when the coupling exceeds about 30 per cent, and die away with a very little reduction in the coupling, leaving the predominant free secondary oscillation as the survivor. These curves show how very quickly the primary spark is quenched when using the impact discharger. If the maximum secondary current is set up as ordinates in terms of the coupling as abscissa we obtain curves which rise up quickly to a maximum value and fall again, and which indicate that the maximum value of the secondary current is determined both by the coupling and the secondary decrements.

The two previous papers were discussed together.

Mr. A. Campbell observed that the curves in the second paper showed the superiority of the impact method, and remarked that, since the losses at low frequencies were so exactly proportional to the square of the voltage, it was surprising the same was not true at high frequencies.

Mr. Duddell also expressed surprise that with low voltages the losses were not proportional to V, and drew attention to the importance of knowing exactly where all the energy losses in the secondary occurred.

Mr. E. H. Rayner remarked that a more accurate way to test the results was to plot the power factor against the voltage.

Mr. Addenbrooke said he thought the variation of the losses with temperature was very great, and should be taken into account.

Dr. Eccles pointed out that it was only after the primary spark was quenched that it was possible for the secondary circuit to emit its natural frequency.

Prof. G. W. O. Howe exhibited oscillographs showing the oscillations in the primary and secondary circuits before and after the primary spark had died down.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, February 6th, 1911.

Mr. E. Grant Hooper in the Chair.

"*Chemistry of the Lead Chamber Process.*" By F Raschig, Ph.D.

It was shown by Davy in 1812 that SO_2 and the red vapour from N_2O_4 do not interact except in the presence of water. The formation of chamber crystals (nitrosulphonic acid) is an intermediate step in this action, and their decomposition by an excess of water liberates a fresh quantity of nitrous gases. If in addition to sulphur dioxide and nitrous gases, oxygen (or air) and water be available, the conversion of the SO_2 into sulphuric acid is complete. Chamber crystals, however, can never be observed when the chambers are working normally, and the various assumptions necessarily to Davy's theory are not true in practice.

The chamber gases, it is obvious from their colour, contain more nitric oxide than is required by the relation $NO + NO_2$. Finally, nitrosulphonic acid does not dissolve without decomposition in sulphuric acid as dilute as is found in the Glover tower, but nitrosulphonic acid, a reduction product of nitrosulphonic acid, is for some considerable time stable in sulphuric acid of sp. gr. 1·6; *i.e.*, acid containing 70 per cent of H_2SO_4. This reduction product imparts a characteristic blue colour to its solutions, and its copper salts are coloured an intense blue. From these observations we must draw the conclusion that nitrosulphonic acid, as an intermediate product in the formation of sulphuric acid by the chamber process, must be left out of consideration, inasmuch as the process continues in concentrations of sulphuric acid from 60 per cent at the end of the chambers, to 80 per cent in the Glover tower, and in the latter case the temperatures concerned are such that even a temporary formation of nitrosulphonic acid is out of the question.

The assumption is almost forced on us that in nitrosisulphonic acid we have the true intermediate product of the chamber process. All experiments lead to the conclusion that when air reacts on nitric oxide, two different substances are successively formed. The first, which is produced after a very short time, dissolves in acids or in alkalis to nitrous acid; behaves, in fact, as if it were nitrous anhydride, N_2O_3. The second, which demands for its complete formation about 100 times as long, dissolves in acids and alkalis, half to nitrous and half to nitric acid; behaves as though it were N_2O_4, and reacts with water according to the equation $N_2O_4 + H_2O = HNO_2 + HNO_3$. It must be admitted, then, that the nitrogen compound effective in the chambers is nitrous acid, HNO_2, which exists dissolved in the tiny droplets of sulphuric acid which as mist fill the chamber; and the question of the chemical nature of the chamber process narrows itself to the inquiry, how, under chamber conditions, that is to say, in presence of air, water, and much sulphuric acid of 60 to 80 per cent, does sulphur dioxide react on nitrous acid? Is nitrosisulphonic acid really formed under these circumstances?

The author shows experimentally, first, that sulphur dioxide does not react on nitrosulphonic acid; second, that sulphur dioxide reacts on nitrous acid, which is dissolved in sulphuric acid of the concentrations which occur in the chambers, with formation of nitrosisulphonic acid, which later breaks up into sulphuric acid and nitric oxide. Only one question remains to be answered, though that is an important one: How is nitrosisulphonic acid, H_2NSO_5, formed from sulphur dioxide, SO_2, and nitrous acid, HNO_2? He also shows that when nitrosisulphonic acid is formed from sulphur dioxide and nitrous acid, nitric oxide gas is evolved. The remaining link of the chain is forged. The formation of sulphuric acid in the chambers occurs in this way, viz., the nitrosisulphonic acid formed dissociates into sulphuric acid and nitric oxide, and finally the nitric oxide, with air and water, becomes oxidised to nitrous acid. In the chemical sense, however, we are far from having finished. We ask further: What is the mechanism of the reaction by which, from 2 molcules of nitrous acid and 1 molecule of sulphur dioxide, nitrosisulphonic acid is formed? A chain of experimental evidence is adduced, which by a reduction of the processes going on in the chambers to well known and frequently observed properties of nitrogen compounds satisfies the last desire which the new theory of the chamber process still left to us. That theory can now be expressed in four equations, from the integral of which the catalyst disappears, and there remains an oxidation of sulphur dioxide by means of water and oxygen to sulphuric acid.

$$2NO + H_2O + O = 2HNO_2 \quad . \quad . \quad . \quad . \quad . \quad 1.$$
$$HNO_2 + SO_2 = ONSO_3H \quad . \quad . \quad . \quad . \quad . \quad 2.$$
$$HNO_2 + ONSO_3H = NO + H_2NSO_5 \quad . \quad . \quad . \quad 3.$$
$$H_2NSO_5 = NO + H_2SO_4 \quad . \quad . \quad . \quad . \quad 4.$$
$$SO_2 + O + H_2O = H_2SO_4$$

Not only does the new theory account for various abnormal conditions observed in the working of the chamber process, but by its application it was possible to predict a peculiarity of the chamber process, namely, the possible formation of ammonia, of which no one had thought, or on the basis of the older theories could have thought.

RÖNTGEN SOCIETY.

PROF. WERTHEIM SALOMONSON, of Amsterdam, was the lecturer at the meeting of the Röntgen Society on February 2nd. His subject was the Induction Coil, but he restricted himself to his own oscillographic research—using the high-frequency pattern of the Duddell instrument—upon the behaviour of coils under varying working conditions. His oscillograms were taken with various well-known coils, and with at first a mercury break working in paraffin oil or alcohol, and afterwards with a mercury jet-interrupter working in gas. He devoted attention separately to the ascending and the descending portion of the curve of the primary current as described in the oscillogram. The form of the ascending part of the curve, which denoted the increasing current strength, was principally determined, he said, by the so-called time-constant of the circuit, the self-induction being divided by the resistance. The rapidity with which the curve rose depended upon the value of the electromotive force of the battery, divided by the self-induction. The descending part of the curve, representing the fall of the current to zero in about one-thousandth of a second at the moment the circuit was broken, was of greater interest, since it was in this phase that the secondary discharge occurred, giving the spark or lighting up the X-ray tube. In all oscillograms the rapid descent of the curve was to be noted, sometimes followed by a few oscillations. His oscillographic study of the descending curve had led him, he said, to the conclusion that if the capacity of the primary condenser were varied the time taken by the primary current to fall to zero varied also; that if the capacity were gradually increased, starting from a very small value, the stopping time of the primary current lessened until a definite capacity had been reached, and that any further increase of the capacity tended to lengthen the flow of the primary current after the commencement of the break.

A considerable portion of Prof. Salomonson's paper was occupied with a study of the oscillations found in the descending part of the curve. These were due chiefly to the secondary sparks, and he showed that the amplitude of the more rapid vibrations depended upon the initial phase difference between the primary and secondary circuits, with a maximum for a phase angle of 90 degrees, and a minimum when there was no phase difference. The primary spark, in his opinion, only slightly affected the intensity of the oscillations.

The number of interruptions per second for the maximum secondary effect was the subject which engaged Prof. Salomonson in the concluding part of his paper. After showing that with very rapid interruptions it was of advantage to reduce their number, and with very slow interruptions to make them more frequent, he pointed out that there must be some intermediate number which gave the best results from the point of view of secondary effect. Mathematical and practical observations had led him to the belief that for coils of 10—12 inch sparking distance the average number of interruptions to be desired was twelve to thirteen per second. Of course this number was only possible with very small voltages, say, up to 18 volts. If the voltages were increased there would be some danger to the coil in reducing the number of interruptions so greatly, and it would be safer to work with a larger number. For the higher voltages, therefore, he formulated a rule, which he admitted was somewhat crude and empirical, but which might serve for practical purposes, that the most advantageous number of interruptions per second for small induction coils was given by the

number representing the voltage, granted that the time-economy of the interrupter were 0·5. With larger coils the number was smaller.

Some radiographs of the thorax were shown which had received exposures of about one-hundredth of a second, a specially powerful coil, the "Unipols," being used for the purpose, and the definition was everything that could be desired.

CORRESPONDENCE.

ASSOCIATION OF TEACHERS IN TECHNICAL INSTITUTIONS.

To the Editor of the Chemical News.

Sir,—The Council of the above Association has recently had under consideration representations from a number of members of the Association in London and Provincial Technical Institutions, part of whose duties consists in the preparation of students in day and evening classes for the Intermediate and Final B.Sc. External examinations of London University. In these representations attention has been drawn to the marked inequality of the requirements of the examiners for a "pass" in the respective subjects, as shown in the great variation in the percentage of passes.

I am directed by the Council to bring the following facts to your notice, and to ask you to place the matter before the Senate and the Council for External Students for their consideration.

The figures in Table I., taken from the recent University Calendars, show that there is a serious discrepancy between the requirements of the various examiners, especially in the case of chemistry, and that as a result serious injustice is there done to students and teachers.

The Council desires to suggest for your consideration, and that of the Senate, that the above statistics show:—

(*a*) That there has been an undue increase in the percentage (34·9 to 60·2) of total failures in the period 1906—1909 inclusive.

(*b*) That in group A (the group of subjects taken by the great majority of the candidates, especially from the Technical Institutions) — (1) The percentage of failure in chemistry has steadily increased from 24·4 per cent in 1907 to 46·9 per cent in 1909. (2) The percentage of failure in chemistry in 1909 and 1910 is disproportionately high as compared with the percentage of failures in the other subjects of the group.

With respect to the above, the Council desires to point out that the educational experience goes to show that with a large number of candidates (about 700 in this case) from all parts of the country, the intellectual standard and training of the candidates, taken as a whole, will vary only to a slight extent from year to year, and therefore the percentage of failures should show a corresponding minor variation only. Further, since the majority of the candidates take the same combination of subjects (Chemistry, Physics, Pure and Applied Mathematics) the high percentage of failures in chemistry, as compared with those in the other three subjects mentioned, cannot be justified.

In this connection we would point out that there has been no alteration in the syllabus of the examination since about 1901.

The Council desire to point out, with respect to the statistics relating to the External B.Sc. Pass Examination (Table II.), that in the period 1905 to 1909 the percentage of failures in chemistry is considerably higher than the corresponding results in the subjects of Group A, namely, Physics, Pure Mathematics, and Applied Mathematics. Further, the percentage of failures in chemistry has increased from 40·8, 1905, to 58·5, 1909, although (*a*) no alteration of syllabus has taken place, (*b*) it is generally admitted that the teaching of chemistry, along with that of other (scientific) subjects, has improved considerably during recent years.—I am, &c.,

P. Abbott, Hon. Secretary.

Table I.—*External Inter. B.Sc.*

		1906.		1907.		1908.		1909.	
		Entries.	Per cent failure.	Entries.	Per cent failure.	Entries.	Per cent failure.	Entries.	Per cent failure.
A.	Chemistry	755	21·2	688	24·4	664	32·7	761	46·9
	Physics	745	10·3	670	19·9	631	19·7	740	30·7
	Pure Mathematics	734	8·3	703	11·5	663	23·5	767	25·3
	Applied Mathematics	579	25·9	556	23·6	495	15·8	627	14·4
B.	Botany	206	14·1	180	33·3	179	35·8	161	47·8
	Zoology	78	24·4	52	38·5	77	19·5	52	28·8
	Geology	110	16·4	93	8·6	89	15·7	98	14·3
	Total candidates	806		738		703		805	
	Per cent failure	34·9		42·3		47·5		60·2	

Table II.—*External Final B.Sc. (Pass).*

		1905.		1906.		1907.		1908.		1909.	
		Entries.	Per cent failure.	Entries.	Per cent failure.	Entries.	Per cent failure.	Entries.	Per cent failure.	Entries.	Per cent failure.
A.	Chemistry	130	*40·8*	165	37·0	130	*43·1*	146	*52·1*	159	*58·5*
	Physics	182	16·5	238	32·8	196	36·7	212	42·9	233	30·5
	Pure Mathematics	186	31·7	242	26·0	207	23·2	214	36·0	263	35·4
	Applied Mathematics	100	22·0	132	25·8	107	20·6	107	49·5	133	42·1
B.	Botany	29	17·2	45	35·6	52	48·1	51	37·3	45	33·3
	Zoology	10	20·0	9	33·3	9	11·1	6	0	7	14·3
	Geology	25	11·0	24	17·6	23	30·4	28	10·7	25	16·0

Physical Society.—We are informed that owing to an alteration in the publications, papers read before the Physical Society of London in future will appear in general only in the *Proceedings* of the Society and not in the *Philosophical Magazine*. The *Proceedings* and other publications are now obtainable by the public from the publishers to the Society, the *Electrician* Printing and Publishing Company, Ltd., 1, 2, and 3, Salisbury Court, Fleet Street, London, E.C.

OBITUARY.

DR. JULIUS WILHELM BRÜHL, PH.D., D.Sc.,
Professor of Chemistry in the University of Heidelberg.

We regret to announce the death of Professor Brühl at Heidelberg on the 5th inst. The deceased was an Honorary Member of the Royal Institution, and was well known to English men of science, not only by his researches in chemistry, but, personally, by his visits to England. In 1905 he gave a Friday Evening Discourse at the Royal Institution. The subject was on the Development of Spectro-chemistry, and it was treated in a masterly manner, the development of research being reviewed since the time of Newton. The lecture was delivered in English, and all who heard it were struck by the perfect command the lecturer possessed over our language, not only in its classical and more elegant phases, but in its familiar and more colloquial aspects. To listen to Dr. Brühl's conversation few would have noticed that he was speaking a foreign language, and his knowledge of English literature was on a par with his linguistic attainment. In the decease of Dr. Brühl, Chemistry loses a great and successful exponent and many English men of science a valued friend.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 16, 1910.

Bromo-salts of Platinum.—A. Gutbier.—The hexabromoplatinates of aliphatic ammonium compounds, *e.g.*, anilinium hexabromoplatinate, $[C_6H_5.NH_3]_2PtBr_6$, may be prepared by making the ammonium bromide from the base and hydrobromic acid, and then adding it to the hydrogen platinum bromide. The precipitate can be purified by recrystallising from dilute hydrobromic acid. The compounds are mostly only slightly soluble in cold water and more soluble in warm water. They are decomposed by boiling with much water. They are relatively slightly soluble in dilute hydrobromic acid at the ordinary temperature, but are easily dissolved, giving red solutions on heating. The bases are set free from solutions by concentrated caustic soda. Ammonia gives pure yellow solutions at room temperature. Hydrazine hydrate decolorises the solutions in the cold, and sets free nitrogen and platinum on heating.

Chloro-salts of Osmium.—A. Gutbier.—By decomposing sodium hexachloro-osmate with aliphatic ammonium chlorides the corresponding hexachloro-osmates of aliphatic compounds are obtained. They are much less soluble than the sodium salts, and separate in the form of crystalline yellow or red-brown precipitates. They are anhydrous and stable in air. They dissolve in cold water, but the pure aqueous solutions readily decompose. They dissolve in dilute hydrochloric acid, giving stable solutions, and are taken up by alcohol.

Sulphanilide.—A. Wohl and Franz Koch.—A good yield of sulphanilide may be obtained by adding moderately dilute sulphuryl chloride to a large excess of aniline. Sulphanilide readily forms a disodium salt and mono- and diacetyl compounds. Excess of acetic acid anhydride in presence of sodium acetate splits off two molecules of diacetanilide, $C_6H_5.N(CO.CH_3)_2$, and sulphuric acid. In presence of free sulphuric acid aminobenzenesulphonic acid is formed. In order to nitrate sulphanilide it is necessary to exercise great caution, or else the molecule is decomposed. Sulphanilide unites with diazo-compounds in alkaline solution; with nitrous acid it yields diazobenzene nitrate, and with methyliodide dimethyl-diphenylsulphanilide.

MISCELLANEOUS.

New Reaction of Cupreine.—Georges Denigès.—If ammonia (1 cc.), hydrogen peroxide (1 vol.), and copper sulphate (0·1 cc. of a 3—4 per cent solution) are added to 10 cc. of a 0·2 per cent solution of cupreine sulphate a green coloration is produced on shaking, and greenish blue particles are deposited. The mixture becomes a bright emerald green if an equal volume of alcohol is added, or if it is acidified with hydrochloric or acetic acid. —*Comptes Rendus*, clxi., No. 26.

Ammonia for Commercial Purposes.—Prof. Fritz Haber, who has been selected to be the Director of the Physical-Chemical Research Institute that the Emperor William Society intends to establish at Dahlem, in the neighbourhood of Berlin, is known as the discoverer of a new process by means of which the nitrogen of the atmosphere is utilised directly for the production of ammonia. Prof. Haber's patents have been secured by the Baden Anilin and Soda Works, and it is stated that his process has been brought to such technical perfection there that synthetic ammonia will soon be on the market. The practical value of the new method of producing ammonia is expected to be enormous, especially for agriculturists.—*Morning Post.*

NOTES AND QUERIES.

"*" Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Liquid Air Plant.—Can any reader supply names of makers of liquid air plant working on Claude's ddiabatic method?—W. E, S

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Royal Society of Arts, 8. (Cantor Lecture). "Brewing and Modern Science," by Prof. A. J. Brown.
—— Society of Chemical Industry, 8. "Composition of the Acids flowing from the Thompson Displacement Apparatus for the Manufacture of Guncotton," by G. W. MacDonald. "Ammonium Sulphate and its Instability" and "Hydrolysis of Ammonium Salts," by Watson Smith. "Study of some Reactions in Gels," by E. Hatschek. "New Still-water Calorimeter," by J. H. Coste and B. R. James.
TUESDAY, 21st.—Royal Institution, 3. "Heredity," by Prof. F. W. Mott, F.R.S., &c.
WEDNESDAY, 22nd.—Royal Society of Arts, 8. "Water Finders," by Prof. J. Wertheimer.
THURSDAY, 23rd.—Royal Institution, 3. "Problems of Animals in Captivity," by P. Chalmers Mitchell, F.R.S., &c.
—— Royal Society. "Transmission of Flagellates Living in the Blood of certain Freshwater Fishes," by Miss M. Robertson. "Report on the Separation of Ionium and Actinium from certain Residues, and on the Production of Helium by Ionium," by Dr. B. B. Boltwood. "The Secondary γ-Rays produced by β-Rays," by J. A. Gray. "Specific Heat of Water and the Mechanical Equivalent of the Calorie at Temperatures from 0° to 80° C., with Additional Note on the Thermoid Effect," by W. R. and W. E. Bousfield. "Measurement of Specific Inductive Capacity," by Prof. C. Niven.
FRIDAY 24th.—Royal Institution, 9. "Mouvement Brownien et Réalité Moléculaire" (in French), by Prof. Jean Perrin, D.Sc.
—— Physical, 5. "Flames at Low Temperature supported by Ozone," by The Hon. R. J. Strutt. "Movement of a Coloured Index along a Capillary Tube, and its Application to the Measurement of the Circulation of Water in a Closed Circuit," by Dr. A. Griffiths. "Optical Lever of High Power suitable for the Determination of Small Thicknesses and Displacements," by E. H. Rayner.
SATURDAY, 25th.—Royal Institution, 3. "Architecture—the Byzantine and Romanesque Period," by T. G. Jackson.

THE CHEMICAL NEWS.

Vol. CIII., No. 2674.

THE DENSITY OF NITON ("RADIUM EMANATION") AND THE DISINTEGRATION THEORY.*

By Dr. R. WHYTLAW GRAY and Sir WILLIAM RAMSAY, K.C.B., F.R.S., University College, London.

According to the disintegration theory of radio-active change a definite number of atoms of radium break up per second, each evolving an α-particle which ultimately becomes a helium atom, leaving behind lighter molecules which form the gas known as "radium emanation," or niton. The identity of the α-particle after it has lost its electric charge with the helium atom has been convincingly proved by Rutherford and Geiger; and measurements of the volume of helium evolved from niton by Ramsay and Soddy, and from radium in equilibrium with its disintegration-products by Dewar, render it exceedingly probable that in each successive change from radium to radium D only one α-particle is expelled per atom.

If, then, the view is held that the radium atom on disintegration to niton splits up into two parts only, one of which is the α-particle, then the atomic weight of the resulting niton is 226·4 − 4 = 222·4. On the other hand, it may be supposed that the disintegrating radium atom splits up into three or more parts; helium, and two other bodies of higher atomic weight, if three parts. On account of its greater mass, the heavier particle might be expelled below the critical velocity necessary for the formation of ions in the air, and might itself be non-radio-active; if this were the case, its presence in a solid state would almost certainly escape detection. There is no direct evidence against such a supposition, for the atomic weights of none of the products of the disintegration of radium have been determined. Experiment alone can settle this question of the true atomic weight of niton; but on account of the exceedingly small volume of this gas obtainable from a relatively large weight of radium, the experiment is by no means easy.

A number of investigators have sought to obtain the atomic or molecular weight by comparing the rates of diffusion of "emanation" and air or nitrogen.

	Found.
Pierre Curie and Danne (*Comptes Rendus*, 1903, cxxxvii., 1314)	176
Bumstead and Wheeler (*Am. Journ. Sci.*, 1904, p. 97)	180
Rutherford and Miss Brooks (*Trans. Roy. Soc. Canada*, 1901)	176
Makower (*Phil. Mag.*, 1905)	100
Chaumont (*Le Radium*, 1909, vi., 106)	70—100

Perkins compared the rate of diffusion with that of mercury vapour, also a monatomic gas, and found 235 (*Am. Journ. Sci.*, 1908, p. 461).

Lastly, Debierne made use of Bunsen's method of causing the gas to issue through a minute perforation in a diaphragm of platinum, and as the result of a very concordant set of experiments, obtained the number 220 for the molecular weight (*Comptes Rendus*, 1910, cl., 1740).

But none of these methods, however ingenious, can be accepted as conclusive, for the conditions are so different from those usually obtaining in ordinary work that no certain inference can be drawn.

In 1909 we attempted the solution of this problem in another way (*Trans. Chem. Soc.*, xciii., 1073). We found it possible to determine the critical- and boiling-points of niton with less than one-tenth of a cub. mm. of gas. Assuming it to belong to the inactive series of gases, we plotted the critical- and boiling-points of argon, krypton, and xenon against their atomic weights, and found these points to lie almost exactly on a slightly curved line. Extrapolation showed that for the emanation to lie either on the line connecting the boiling-points or the critical-points, it must possess an atomic weight approximating to 176. It was quite impossible to bring the value 222·4 anywhere near the extrapolated curves; but it must be observed that, as the curvature is slight, a small error in the constants of argon, krypton, or xenon might alter the curvature in the reverse direction, and so make more probable the higher atomic weight. We realised at the time that the results could not be accepted as certain, and that the only criterion must be the determination of the density of the gas. It is, however, remarkable that all the determinations quoted, with the exception of Makower's and Chaumont's, point to an atomic weight either of 176 or of 222; these are the tabular atomic weights of the immediate follower of xenon in the Periodic Table, on the one hand, and of the next member on the other. The members of the series are;—

Helium.	Neon.	Argon.	Krypton.	Xenon.	I.	II.
4	20	40	83	130	176	222

To determine the density of a gas, four separate measurements are essential—the volume, the temperature, the pressure, and the weight of the gas. In the present case, however, the problem was simpler, for the volume of niton at normal temperature and pressure accumulating in a given time from a known weight of radium is a constant and invariable quantity, and has been repeatedly measured. In 1908 Rutherford found this volume to be 0·61 cub. mm., per grm. of radium; Debierne in 1909 obtained the value 0·58 cub. mm., and these results were confirmed shortly afterwards by our own work (*loc. cit.*, p. 1082), which gave 0·601 cub. mm. Rutherford has been able to calculate this constant from the result of his beautiful experiment in which he actually counted the number of α-particles emitted from a known weight of radium, and the value found was 0·585 cub. mm. It may therefore be taken as certain that the error in this constant does not exceed 5 per cent. For our experiments this figure is unessential, since the actual volume of emanation from the total radium at our disposal had been measured.

The problem which we have attacked is the determination of the weight of emanation evolved in a given time from our total quantity of radium. The radium bromide solution from which the niton for these experiments was drawn was contained in three bulbs sealed on to a Töpler pump. The maximum measured quantity of emanation which can be extracted with the pump from the solutions in the bulbs is 0·127 cub. mm. By collecting the gas every eight days, the yield was only 76 per cent of this quantity, so that the total volume obtainable for weighing scarcely exceeded 0·1 cub. mm. The weight of this volume on the assumption that the atomic weight is 222, is less than 1/1400 mgrms. It is therefore evident that in order to weigh this minute quantity of gas with sufficient exactness, a balance turning with a load not greater than 1/100,000 mgrm. was a necessity. This seems an almost inconceivably small weight to attempt to measure, when one considers that the limit of sensibility of a delicate assay balance is is about 1/200 mgrm., and that even the Nernst balance will hardly turn with a load smaller than 1/2000 mgrm. (As we shall have to deal with very small weights, it is advisable to adopt a new unit; this is conveniently the millionth of a mgrm. The abbreviation here used for this is μ mgrm.).

The successful construction of a balance capable of weighing these very minute quantities has been accomplished by Dr. B. D. Steele and Mr. Grant, of the University of Melbourne; thanks to their skill and ingenuity, they have constructed an instrument 100 times

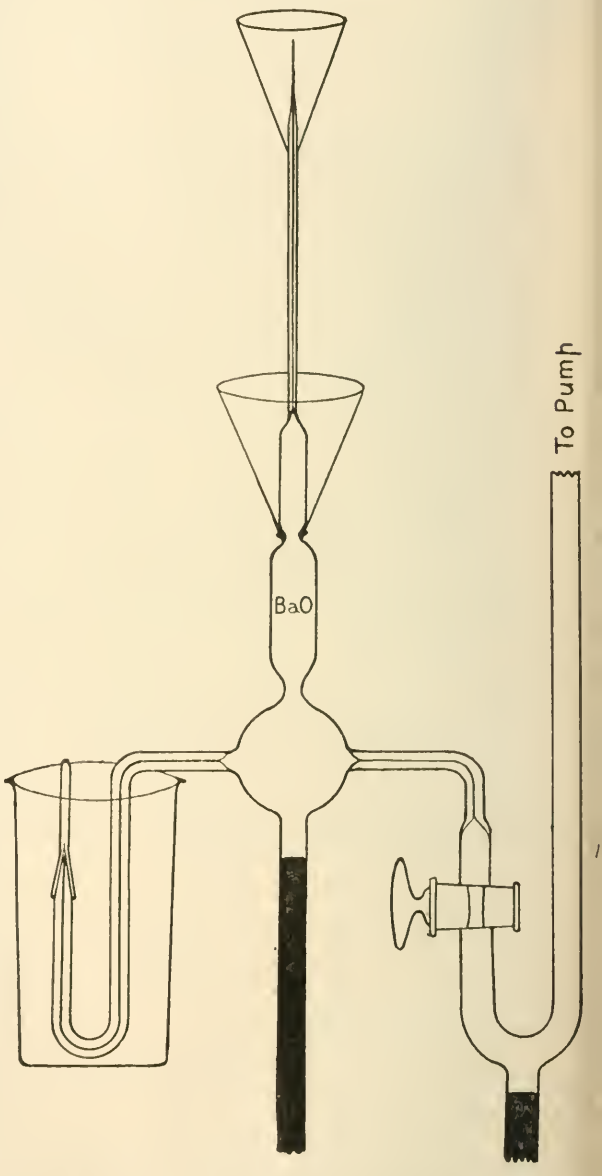
* A Paper read before the Royal Society, January 12, 1911.

more sensitive than the Nernst micro-balance. Steele and Grant have published an account of their balance (*Roy. Soc. Proc.*, 1909, A, lxxxii., 580), and they have shown that a sensibility of 1/250,000 mgrm. could be attained. After several trials we have been successful in constructing a similar instrument and in determining the density of the radium emanation with its help. It is only fair to state, however, that Dr. Brill, working in the laboratory of University College, improved the Nernst balance, so that it turned with 1/10,000 mgrm. The subject was followed up later by Dr. Gwyer, also at University College, who introduced the hydrostatic method of determining small weights, the buoyancy of a small bulb containing a known weight of air being altered by the adjustment of the pressure in the balance case, constructed so that a vacuum could be made. We then corresponded with Dr. Steele, who was so obliging as to inform us of the principle and construction of his balance, then in an experimental stage.

The paper published by Steele and Grant renders a minute description of our balance unnecessary; but our balances (for several were constructed) differ in some small respects from theirs. The beam, for example, was made by placing thin silica rods in grooves carefully ruled on a smooth plane block of graphite, and then fusing the contiguous ends together in an oxygen coal-gas flame; in this way, a symmetrical beam, lying on a plane surface, was secured. If this condition is not fulfilled, the beam is apt to be deformed by small stresses set up in the quartz at the points of junction, as found by Steele and Grant. It is also necessary that the knife-edge shall be at right angles to the beam in two planes. This was managed by sealing the knife-edge on to the beam with a long guiding rod of silica attached to it, so that adjustment to a right angle is not difficult by trial and error; this guiding-rod, when fused off, left a stem of a few mm. in length, to which the platinised silica mirror was fused. By this device the mirror revolved without displacement when the balance was deflected. Another improvement was the direct sealing of a fine quartz fibre to the end of the beam, whereby a much freer suspension was attained. Again, while Steele and Grant weighed by displacement of the zero, our weighings were made by a null method, whereby the alteration of pressure brings the spot of light to its original position. In this way, any possible variation in the sensibility of the beam with its deflection from horizontality is avoided. To eliminate as far as possible temperature changes and also vibration, the balance is mounted on a stone pillar in a cellar, and the brass case stands inside a large box of bright tin-plate. The mirror is illuminated by a beam of light from a Nernst lamp, which reflects on to a mm. scale about 3 metres away. The light is allowed to impinge on the mirror only when a reading is taken.

The small counterpoise quartz bulb, which contains a known weight of air, serves instead of a set of weights. When the air pressure in the balance case is the same as that in the bulb the apparant weight of the air which it contains is nil. That is to say, the real weight of the air in the bulb is exactly counterpoised by the buoyancy of the air outside. In a vacuum the sealed up air exerts its full weight, and at any intermediate pressure the arm of the beam carrying the bulb is loaded with a known fraction of this weight. The counterpoise bulb of the balance used by us has a capacity of 22·2 cub. mm., and the air which it contains weighs 0·027 mgrm., or 27,000 μ mgrm. (millionth mgrms). A pressure change of 1/10 mm. can be easily read by a cathetometer, so that any object lighter than 27,000 μ mgrm. can be weighed with an accuracy of 3·55 μ mgrm.

By reading the pressure more exactly, say, to 1/100 mm., the limit of accuracy could have been increased to one-tenth of the figure above, provided, of course, that the sensibility of the balance is great enough; to obtain this maximum degree of sensibility two important conditions have to be fulfilled. The centre of gravity of the beam must be most carefully adjusted, and the knife-edge must be perfectly straight and regular, even when viewed through a microscope with a half-inch objective. The final adjustment of the centre of gravity is made by volatilising away from the top of the centre rod, round which the beam is built, minute quantities of quartz in the oxy-coal gas blowpipe; this is a comparatively simple process. The making of the knife-edge gave a good deal of trouble, but in the end this difficulty was overcome. The edge itself is about 0·3 or 0·4 of a mm. long, and is ground in the form of a



right-angled prism on the end of a quartz rod, which is subsequently fused on to the beam. The grinding and polishing of the edge, which is a very delicate operation, was carried out for us by Messrs. Hilger and Co.

Our present balance is sensitive to about 2 μ mgrm.; its zero remains perfectly constant for days together. When the counterpoise bulb is removed, the zero of the balance is not altered by large changes of pressure within the case.

The standard of weight, which is, of course, the weight

of the air in the counterpoise bulb, has been verified in the following way:—A long measured length of very fine aluminium wire was weighed as accurately as possible on an assay balance. A small portion of this wire, about 2 mm. in length, was cut from the longer length in such a way that the cross-sections were as nearly as possible circular; it was then measured under a reading microscope, and its weight was determined in terms of the counterpoise-bulb on the micro-balance. The weight so determined agreed within 1 per cent with the weight calculated, on the assumptions that the wire was uniform and that the weight of the small piece was directly proportional to its length.

For the measurement of the density of very small quantities of niton or of other gases, the following procedure was adopted:—The gas, of a volume of the order of 0·1 cub. mm., was forced by means of mercury into a fine capillary tube of about 1 mm. external and 0·2 mm. internal diameter, which was sealed on to the apparatus for purifying the gas (see Fig.). The upper end of this tube was drawn out into a finer very thin-walled tube, the extreme point of which was sealed. When necessary, the volume of the gas was measured at various pressures in the capillary tube, carefully calibrated for this purpose. After measurement, the tip of the tube was surrounded for some minutes with liquid air, in order to condense the gas; the volume of the gas was then considerably increased, so that any hydrogen still present should expand, and only a minute trace could remain at the top of the tube; the tube was then sealed at a distance of about 20 mm. below the tip, by aid of a pin-point gas flame. After most carefully cleaning and drying the small tube, it was lifted with platinum-tipped forceps, the tips of which had just been heated to redness, and placed in a little tightly-fitting bucket, or external tube, of silica, suspended from one arm of the balance by quartz fibre; the pointed end of the density-tube was downwards, and the lower end of the bucket was slightly curved. A quartz counterweight suspended to the same arm of the balance was then adjusted, by fusing on or by volatilising off small pieces of silica, so that the beam was in balance at a pressure in the neighbourhood of 50 mm. After an hour or more the pressure in the case was exactly measured, and the position of the spot of light on the scale was noted. The bucket and tube were then removed with the platinum-tipped forceps; and, while it was held vertical inside a wider tube, the density-tube was pressed down with a glass rod, cup-shaped at the end; the drawn-out point of the density-tube broke, but no splinters of glass could escape, for they were all retained in the bucket of silica. The bucket and its tube were then replaced on the balance, and the air was exhausted; air was again admitted, and a second exhaustion was made; in this way the gas was removed from the interior of the density-tube, and replaced by air. The pressure was then adjusted to bring the zero-point back again to its original position. With practice, the whole operation could be carried out in less than five minutes; this reduced the chance of error from the condensation of moisture on the glass and the settling of dust particles.

Before experimenting with the precious niton, the method was tested with the less valuable xenon. Before freezing the gas its volume was measured; it amounted, at 0° and 760 mm., to 0·0977 cub. mm. It was then frozen, and the density-tube was sealed off and placed in its bucket on the balance; after breaking the tip, the pressure change was 17·1 mm. (70 − 52·9); the temperature change was too small to affect the result; this pressure change corresponds to an apparent loss of weight of 608 μ mgrms. But this number does not represent the real weight of the xenon, for in the second weighing the tube is full of air, and therefore to the observed weight the weight of the air filling the tube at the temperature and pressure of the second weighing has to be added. The volume of the tube being known (for its length was measured), the weight of air under the conditions of weighing (52·9 mm. and 16°) proves to be 46 μ mgrms.; hence the total weight is 654 μ mgrms. A further correction has next to be applied to allow for the difference in buoyancy of the glass of the weighing-tube in the two weighings. This correction could, of course, be calculated, provided one knew the weight of the tube, the density of the quartz of the silica counterpoise on the end of the beam opposite to the objects to be weighed, and the density of the sample of glass forming the weighing-tube. It was found, however, to be more accurate and convenient to determine directly on the balance the magnitude of this correction for each experiment. For this purpose the counterpoise bulb containing air was replaced by a piece of quartz of almost exactly the same weight, and under the new conditions the variation of the zero point of the balance for a given change of pressure was determined. Knowing the weight corresponding to each scale-division displacement of the zero-point, the variation in buoyancy of the open glass tube between the two weighings was easily and accurately calculated. In general, this correction is a somewhat large one, and amounts in this case to no less than one-seventh of the total weight of the gas. The reason for this is the large difference in weight between the density-tube and the contained gas. The density-tube, as a rule, weighed about 30 mgrms., and the contained gas about 1/2000 mgrm.; hence the weight of the gas is to that of the vessel as 1 to 60,000, whereas, under ordinary conditions, when weighing 200 cc. of gas, the ratio is about 1 to 600.

In this experiment, the correction for the buoyancy of the glass proved to be 91 μ mgrms.; but there is still a correction to be applied, for there is a change of buoyancy due to the volume occupied by the gas itself. As the volume of the tube was known, this could be calculated with greater accuracy than it could be determined by experiment. In this case, the xenon occupied 0·536 cub. mm., and the difference in buoyancy of the air between the pressures 70 and 52·9 mm. (17·1 mm.) is $17{\cdot}1 \times 0{\cdot}536 \times 1{\cdot}29/760 \times 1000 = 15$ μ mgrms. Had the sealed tube been weighed at the lower instead of the higher pressure (at 52·9 instead of 70 mm.), it would have weighed more; hence this correction is positive. The true weight of the xenon is therefore $654 - 91 + 15 = 578$ μ mgrm. The calculated weight of 0·0977 cub. mm. of xenon is 577 μ mgrms. The exact agreement is doubtless a coincidence.

With niton, two sources of error made their appearance; in the first place, the density-tube became strongly electrified, and attracted dust particles and adsorbed air, and in the second, the tube was always at a higher temperature than the surrounding atmosphere during weighing (see Ramsay, *Trans. Chem. Soc.*, 1907, xci., 931), and convection currents were liable to be set up in the air surrounding one limb of the balance. The first of these effects could not be entirely eliminated, but it was considerably reduced as regards dust by filtering the air through a long column of tightly packed cotton-wool before allowing it to enter the balance-case. In addition, the tube, after suspension from the beam of the balance, was, as a rule, gently heated by passing a non-luminous pin-pointed gas-flame quickly over its surface, thus burning off most of the attracted particles of dust. The same expedient was also adopted, before the second weighing, after the tube had been broken. Blank experiments showed that this procedure did not alter the weight of the tube in the slightest degree, provided it was perfectly clean; when dust particles were present, however, there was always a small loss of weight.

The effect of convection currents was reduced as much as possible by weighing at a low pressure; in our five experiments, the final pressure varied from 87 to 13 mm.; and the concordance of the results precludes the possibility of any serious error from this source. It may also be noted that the density-tube, after removal of the niton, and during the second weighing, contained approximately the equilibrium amount of radium A, B, and C, the heating effect of which is a large fraction of the total heating effect of the emanation in equilibrium with its quick-change pro-

ducts; hence any error in the first weighing was partially compensated by a similar error in the second weighing. Finally, we would point out that convection currents, on account of the position and shape of the tube, have very little influence on the balance, and their presence should have been revealed by the oscillations of the beam and the position of the zero-point. No irregularity, however, was noticed, and we believe that this source of error produced only negligibly small effects.

(To be continued).

OXIDATION IN SOIL.*

By M. X. SULLIVAN and F. R. REID.

(Concluded from p. 75).

Influence of various Salts with and without Certain Organic Acids and their Salts.

ARIOUS salts of manganese. iron, aluminium, calcium, nd magnesium have a greater or less oxidative action on a water solution of aloin. Accordingly, manganese in the form of the sulphate, chloride, carbonate and dioxide, iron as ferric chloride, aluminium as the oxide and the hydrate, calcium as carbonate, and magnesium as carbonate, were added to various soils in the ratio of 100 parts of the metal to one million of soil, with and without the presence of organic acids and their salts. Manganese dioxide increased the oxidative power of the soils somewhat. All the other salts had little effect on the oxidative power of the soil, except in the presence of glycolic, tartaric, malic, and citric acids, and sodium citrate and tartrate. The best oxidation occurred in soils to which manganese and citric acid had been added.

Whether or not the oxidising principle in the soil is manganese or other salts which are activated by the organic hydroxy acids in the incinerated soils and are rendered more effective in the normal soil, it seems most probable that the oxidising power of the soil is due not to enzymes, but to a combination of inorganic constituents with definite kinds of organic matter. Since true enzymes readily undergo decomposition in solution, we should expect them to undergo decomposition readily in the soil.

Influence of Various Factors in Soil Oxidation.

Water Content.—The oxidation by the soils at optimum moisture is always considerably greater than that of the soils in air-dried condition.

Surface Soil compared with Sub-soil.—Of twenty-two soils which had more or less power to oxidise aloin, samples of the corresponding sub-soils were tested. Of these sub-soils, sixteen possessed no oxidising power, three oxidised the aloin to a slight degree, two oxidised the aloin more than the soil did, and one equalled the oxidising power of the soil.

Effect of Cropping.—The effect of cropping on soil oxidation is variable.

Effect of Fertilising and Cropping.—To test the effect of fertilising and cropping, wheat was planted in the various soils, and allowed to grow for seventeen days. If the oxidative power of the fertilised and planted soil is determined immediately after the crop is removed, the planted soils tend to give a turbid solution, and the comparative oxidising power of the soils cannot be measured. If, however, the oxidative test be made ten to fifteen days after the crop was removed, the fertilised and planted soils show the greater oxidative power.

Effect of Fertilisers.—Numerous experiments have been made on the effect of fertilisers on the oxidative power of soils with results that show that the fertilisers sometimes increase oxidation, sometimes decrease it, and that the effects of the fertilisers are different in the different soils.

The action of the fertilising salts must be attributed to the effect they have on the micro-organisms of the soil, modifying their numbers and activities with a resulting modification of biochemical activities, and a resulting change in both the amount and the condition of inorganic and organic soil constituents, or directly on the soil constituents, especially in the organic matter which is undergoing change by autoxidation, or as a result of the activity of micro-organisms. In short, the fertilisers added to soil or present in soils do work and bring about various changes, one of which is made manifest by the changed oxidative power.

The Relation of Organic Matter to Soil Oxidation.

Oxidation in soils is undoubtedly due to various factors, and is dependent not only on the inorganic constituents of the soil, but also on the organic matter. In the case of the Hagerstown loam, the manured soil had by far the best oxidising power. With the unfertilised soil as 100, the plot which had received ten tons of stable manure to the acre was 136 and over. Decomposing cowpea vines added to sassafras silt loam increased the oxidising power. When various soils were steam-heated or heated at 105° C. for an hour, the oxidative power was greatly lessened. This decrease in the oxidising power we have found to be due mainly to changes in the organic matter. When the organic matter of the soil was destroyed by incineration, the oxidising power was lost. The oxidative power of the soil is dependent on the nature of the organic matter. Thus, when salts of manganese, iron, calcium, magnesium, and aluminium were added to soil of slight oxidative power, oxidation was but slightly increased until certain kinds of organic matter were added, such as citric, malic, tartaric, glycolic acids, or their salts. These compounds we found had a reducing action, converting ferric compounds to ferrous compounds, and probably bring about the stimulation of the oxidative power of the bases mentioned by means of a preliminary reduction to lower, less oxygenated compounds, which, in turn, re-oxidising themselves, activate the oxygen of the air. This active oxygen oxidises other bodies such as organic material of the soil or aloin which is employed as a test of oxidation. It may be, too, that hydroxy acids affect the oxidative powers of complex organic substances or of inorganic-organic complexes.

Fresh plant juices have the power to oxidise aloin directly. On standing, this direct oxidising power is often lost, either because of change in the reaction of the juices or because the oxidising principles have undergone changes. After the loss of the direct oxidising power, the plant juices, as a rule, have an indirect oxidising power; that is, they can oxidise with the addition of hydrogen peroxide.

The addition of hydrogen peroxide increased the oxidising action of some soils, decreased it in others. The peroxide increased the oxidative power of Takoma lawn soil and Cecil fine sandy loam which give no direct oxidation of aloin, and decreased oxidation in Sassafras silt loam and Hagerstown loam, manured, which normally oxidise aloin directly. It is possible that the soils which normally give a direct oxidation of aloin contain both organic and inorganic peroxides. It is highly probable that soils rich in organic matter would contain organic peroxides, since such soils have been found by us to have the ability to absorb oxygen. Decomposing cowpea was found to have a strong oxidising power on aloin, an oxidising power which was not entirely destroyed in ten minutes' heating on a steam-bath, or by carbon bisulphide. That organic bodies will form peroxides in the presence of air is shown by Baeyer and Villiger (*Ber.*, 1900, xxxiii., 1569), who showed that when benzaldehyde is oxidised by atmospheric oxygen, benzoyl peroxide is formed, $C_6H_5CHO + O_2 = C_6H_5COOOH$, and by Ditz (*Chem. Ztg.*, 1905, xxix., 705), who found that ethyl ether in contact with air forms within itself more or less ethyl peroxide.

* Contribution from the Laboratory of Soil Fertility Investigations. Published by permission of the Secretary of Agriculture. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 1.

This ethyl peroxide he found had a stronger oxidising action than hydrogen peroxide.

Bach (*Comptes Rendus*, 1897, cxxiv., 951) concluded that the so-called oxidising ferments in blood are simply readily oxidisable substances having a special aptitude for forming peroxides which oxidise other substances more difficult to oxidise.

Kastle and Loevenhart (*Am. Chem. Journ.*, 1901, xxvi., 539), in discussing the nature of the oxidising ferment of the potato, concludes that the so-called oxidising ferment is in all probability not a true ferment, but an organic peroxide. They further conclude that oxidation phenomena occurring in plants, and probably also in animals, can be satisfactorily explained upon the supposition that the readily autoxidisable substances which they contain are oxidised to the peroxide condition by molecular oxygen, and that the peroxides thus formed in turn give up part, if not all, of their oxygen to other less oxidisable substances present in the cell. In other words, the process of rendering oxygen active by the living cell is probably brought about in essentially the same way that this is accomplished by phosphorus, benzaldehyde, and other oxygen carriers; that is, it is one phase of autoxidation.

Peroxide-forming bodies, such as benzaldehyde and peroxides like quinone, have a strong oxidising action on aloin, both in solution and in soil.

It is possible that, in the soil, complex autoxidisable substances are formed in the changes brought about by the action of micro-organisms on plant *debris*, &c. These autoxidisable substances would combine with the oxygen of the air in much the same way that benzaldehyde does, and would form complex, more or less unstable, peroxides which in turn would give up a part or all of their oxygen to oxidisable substances in contact with them, or could further oxidise themselves.

The possibility of the formation of peroxides in soil even to excess is indicated by Sjollema and Hudig (*Expt. Sta. Record*, 1909, xxi., 115), who found that oat-sick soils were restored to a good condition by manganese sulphate, and suggested that oat-sickness may be due to the formation in the soil in the presence of excess of calcareous fertilisers and physiological alkaline fertilisers as nitrite of soda, of large amounts of peroxides injurious to plants. The favourable action of the manganese sulphate is due, according to these investigators, to the catalytic decomposition of such injurious peroxides.

The Effect of Excessive Oxidation.

Whatever induces excessive oxidation in soil or plant it would undoubtedly be injurious. Thus Woods found that excess of the oxidising enzymes in plants destroyed the chlorophyll (*loc. cit.*). Loew and Sawa (*Bull. Coll. Ag. Tokyo*, 1902-3, v., 161) and Salomone* (*Le Staz. Sper. Agr. Ital.*, 1905, xxxviii., 1015; 1907, xl., 97) found that an excess of manganese sulphate added to soil decreased the growth of plants with a great increase of the oxidative power of the plant juices, and according to Kastle and Elvove (*Am. Chem. Journ.*, 1904, xxxi., 195) strong oxidising agents like nitrates, nibrobenzene, picric acid, chromates, chlorates, arsenates, organic peroxides, and peracids are poisonous to life. In small amounts these substances may be stimulative to life functions. In a similar manner, quinone, a strong oxidiser, is poisonous to plants such as wheat. Under normal conditions, as in the plant, the excessive formation of peroxide is prevented in some way, either by the further oxidation of the peroxides or by the catalytic or peroxide-splitting power of the soils. Most soils have this catalytic power to a greater or less degree, and, in general, we have found that fertile soils have a greater catalytic power, as well as a greater oxidative power, than infertile soils. The relation between oxidation and catalysis is not as clear as it might be, even in the plant where it has been extensively studied.

According to Chodat (*Schweiz Wochenschr. Chem. u. Pharm.*, 1905, xliii., pp. 626, 642, 655), the only property of the catalase of which we have certain knowledge is its power to decompose hydrogen peroxide to water and molecular oxygen. According to Loew (*Report*, lxviii., U.S. Dept. Agr. 1910), Herlitzka (*Rend. Sci. Fis. Mat. et Nat. Real. Acad. Lincei*, 1907, xvi., 473, Series 5, Part II.), Battelli and Stearn (*Comptes Rendus*, 1905, cxli., 1044), and Shaffer (*Am. Journ. Physiol.*, 1905, xiv., 299), on the other hand, the catalase of plants has a protective influence against excessive oxidation. The catalytic power of the soil may, in time, be shown to have a similar action in promoting normal oxidation in soils, and like oxidation may be connected with soil conditions adapted to the growth of the majority of plants.

In the study of oxidation in soils, we have found that most soils will directly oxidise substances in the manner of an oxidase, while a few will oxidise only in the presence of hydrogen peroxide, like the peroxidase reaction in plants and animals. The addition of certain organic hydroxy acids increases oxidation in soils in a way analogous to the activating action of alfalfa laccase and salts of hydroxy acids as discovered by Euler and Bolin (*Zeit. Physiol. Chem.*, 1908, lvii., 80; *Zeit. Phys. Chem.*, 1909, lxix., 187). Dilute mineral acids and alkalis check oxidation in soils as they do the oxidation by plant roots or plant juices. The addition of various salts to soils increases the oxidising power of soil just as Bach (*Ber.*, 1910, xliii., 364) found mineral salts further oxidation changes of tyrosine by tyrosinase. Again, most soils have more or less catalytic power. In short, it would be found undoubtedly that all the various kinds of oxidation going on in plants and animals could be duplicated by a detailed study of oxidation in soil. The oxidation in soil *per se* is due mainly to non-enzymotic forces, inorganic and organic, working separately, conjointly, or in reinforcing or activating combination. In soil oxidation the nature of the organic matters seems to be of great importance. Conjointly with the oxidation in soils which is active whether the soil is planted or unplanted is the oxidising power of the roots.

Conclusions.

1. Soils have the power to oxidise aloin.
2. This oxidising power is increased by adding water to optimum moisture, by the commonly used fertilisers in conjunction with plant growth, by salts of manganese, iron, aluminium, calcium, and magnesium, in the presence of simple organic hydroxy acids.
3. Oxidation in soil is comparable to oxidation in plants and animals.
4. The oxidative power of the soil appear to be mainly non-enzymotic, the results of interaction between inorganic constituents and certain types of organic matter. It may be brought about by organic matter in a state of autoxidation, and by inorganic oxygen carriers such as manganese and iron.
5. Oxidation is greater in the soil than in the sub-soil.
6. Oxidation is greater in fertile soils than in infertile soils.

Royal Institution.—On Tuesday next, February 28, at 3 o'clock, Dr. A. E. H. Tutton begins a course of three lectures at the Royal Institution on "Crystalline Structure: Mineral, Chemical, and Liquid"; on Thursday, March 2, Mr. A. C. Benson delivers the first of two lectures on "Ruskin"; and on Saturday, March 4, Prof. Sir J. J. Thomson commences his course of six lectures on "Radiant Energy and Matter." The Friday Evening Discourse on March 3 will be delivered by Dr. F. A. Dixey, on "Scents of Butterflies"; on March 10 by the Hon. Charles A. Parsons, on "Recent Advances in Turbines"; and on March 17, by John H. Balfour Browne, on "Water Supply."

* In connection with the excess of manganese in soil and soil oxidation see also Kelley, Hawaii Sta. Press, *Bull.*, xxiii. *Journ. Ind. Eng. Chem.*, 1909, 533; Guthrie and Cohen, *Agr. Gazette of New South Wales*, 1910, xxi., 219).

REPORT ON CHEMICAL CONSTITUTION AND THE ABSORPTION OF LIGHT.*

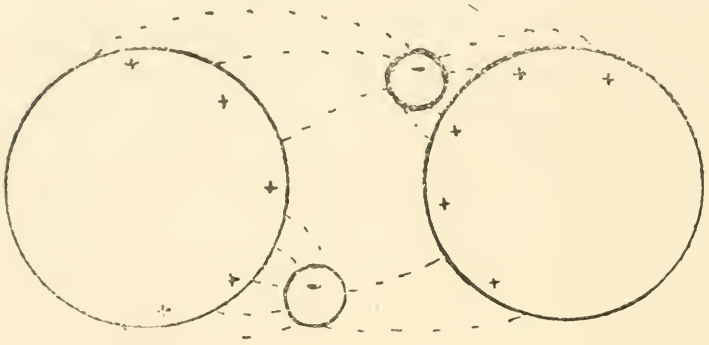
By W. W. STRONG.

(Concluded from p. 77).

Theory of Stark.

STARK (*Zeit. Phys.*, 1908, ix., 85) considers that chemical valency can be explained as due to the presence of negative electrons that hold the positive parts of atoms together. In Fig. 1 it is seen how this can take place, the dotted lines representing lines of electric force.

The conditions represented in Fig. 1 are such that there is very little stray electric field beyond the atoms. Under such conditions the valency electrons are saturated, and



IG. 1.

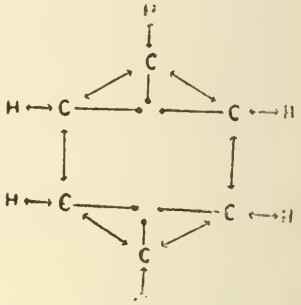


FIG. 2.

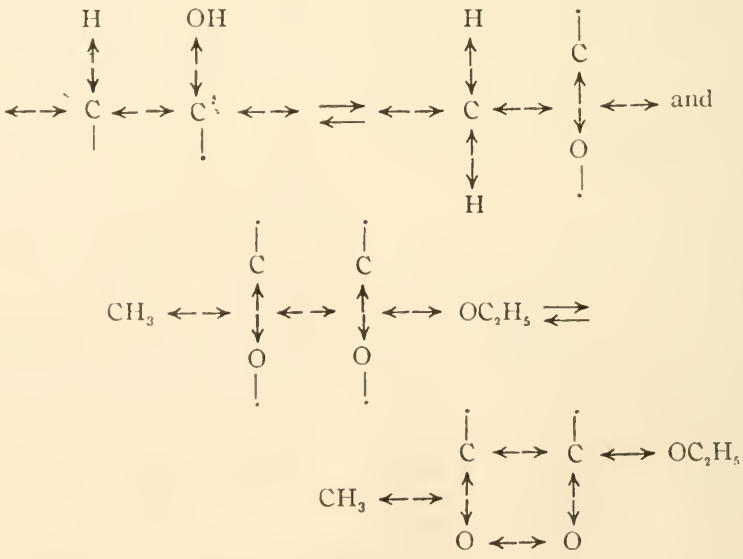


FIG. 3.

Stark represents this by the symbol ⟷. Under many conditions, however, the valency electrons are not so closely united to the atoms and are more or less unsaturated. Under certain conditions an electron may be thrown off the atom, and Stark considers that it is under some condition such as this that selective absorption of light takes place. When the electron returns to the atom it will undergo certain accelerations along its path, and during these accelerations it will emit radiations. Stark believes that under some condition at least similar to this, the fluorescent radiation is emitted and that the period of this radiation will depend on the amount of energy set free when an electron recombines with the positive part of the molecule. From the heat changes which occur in various chemical reactions, Stark calculates what the approximate period of these radiations should be, and in many cases obtains values which agree with the positions of known bands in the spectrum. Among these bands is the ultra-violet band of benzene. Stark's formula for benzene would be that given in Fig. 2.

The symbol —· simply means that one electron is not as closely joined as the other three to the carbon atom It is possible that even this unsaturated electron may have lines of force running to the other carbon atoms. In this way partial valency can easily be explained. The keto-enolic isorropesic changes, as interpreted according to Stark's theory, are represented in Fig. 3.

In this consideration of atoms it would be expected in general that the space containing the electric field of the electron would more or less envelop the positive nuclei of the atoms, and that the volumes of atoms would depend

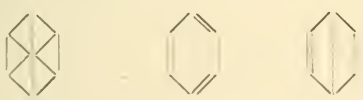
* This Report is based upon an article by H. Ley, entitled "Ueber die Beziehung Zwischen Lichtabsorption und Chemischer Konstitution bei Organischen Verbindungen." See *Jahrbuch der Radioaktivität und Elektronik*, 1910, vi., 274. From the *American Chemical Journal*, xliv., No. 1.

on their valency. This would agree very well with the assumptions of Barlow and Pope (*Journ. Chem. Soc.*, 1906, lxxxix., 1675 ; 1907, xci., 1150 ; Swartz, *Am. Chem. Journ.*, 1907, xxxvii., 638 ; 1909, xlii., 158). These assumptions are as follows: In any chemical body the relative volumes of the atoms are proportional to their valencies; in a crystallised body the atoms are close packed ; in a compound the volumes of the spheres of atomic influences of atoms of the same valency may differ slightly. The latter variation of the sizes of the spheres of influence (interpreted here as the space filled by the electric fields of the valency electrons) may be due to the different amounts of saturation, or, as Stark calls it, the lack of the valency electrons. It would be interesting to know whether the energy relations support this view, it being expected that the greater the lack of the electrons, the less the potential energy of the compound.

Stark and Steubing (*Zeit. Phys.*, 1908, ix., 481, 661) have investigated the fluorescence of a large number of organic compounds. Most spectra are banded, and a band never runs in both directions. The band consists of a tail where the smaller bands are close together. From the tail the small bands may run towards the red or towards the ultra-violet, getting farther and farther apart all the time. But there are never small bands on both sides of the tail. The absorption of light by bands running "to the red" is not accompanied by fluorescence or by any photo-electric effects. The absorption of light in bands running towards the violet (benzene bands) is accompanied by a photoelectric effect, a fluorescence of the bands themselves and by a fluorescence of bands due to the connection of carbonyl, ethylene, or other chromophoric groups, if these be present in the molecule. The addition of more chromophores to the compound shoves the fluorescent bands to the red.

Other Benzene Theories.

There are some colour changes of benzene compounds for which the general theory does not seem to account easily. For instance, nitronaphthalene is yellow. By introducing two nitro groups a colourless compound is obtained. In order to explain phenomena of this kind, Kauffmann (*Zeit. Phys. Chem.*, l., 530; *Ber.*, xxxvii., 2941) assumes that the introduction of groups into a benzene nucleus may change the condition of the benzene ring itself. He considers that benzene may have the diagonal, the Kekulé, or the Dewar formula (*Ber.*, xxxiii., 1725; xxxiv., 682; xxxv., 3668 ; *Zeit. Phys. Chem.*, lv., 547).



I. II. III.

In condition I. benzene has an aliphatic character, as in nitrobenzoic acid, $C_6H_4(NO_2)COOH$. In this condition, having no double bonds, it does not possess strong colour properties. The second condition has an aromatic character, and is exemplified in the phenols. Examples of the third condition are found in aniline, *p*-phenylenediamine, naphthalene, or anthracene. Of the three conditions, the second one is the best chromophore. According to Kauffmann, benzene vapour exists in the diagonal condition, and for that reason it is not luminous when exposed to electric discharges of high frequency or to the rays from radium. Auxochromes and chromophores cause the benzene to become luminous, and for this and other reasons Kauffmann thinks that the condition of the benzene grouping has been changed.

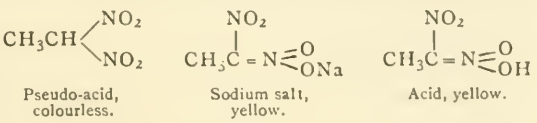
The different changes in colour may be due to one or more of three conditions :—

1. There may be no intramolecular changes of constitution, but the whole change of colour may be due to the change in the radicals.

2. There may be an intramolecular rearrangement.

3. There may be an association of the molecules or compounds formed with the solvent. The above classification includes colour changes that are not explained by isomerism.

In many cases it is practically impossible to decide between the different possibilities. Auwers (*Liebig's Ann. Chem.*, cccl×., 11) and Tuck (*Journ. Chem. Soc.*, 1907, xci., 454) give evidence to show that the sodium salt of hydroxyazobenzene owes its colour simply to the introduction of the sodium. Baly and Schaefer (*Journ. Chem. Soc.*, xciii., 1806), Hantzsch (*Ber.*, xxxii., 575 ; Hantzsch and Veit, *Ber.*, xxxiii., 626; Ley and Hantzsch, *Ber.*, xxxix., 3149), Vey, Gorke (Hantzsche and Gorke, *Ber.*, xxxix., 1073), and others, give some cases coming under class 2. As example, we may take dinitroethane :—



Pseudo-acid, colourless. Sodium salt, yellow. Acid, yellow.

Nitrophenol ether, faintly yellow. Benzene derivative. Chromonitrophenol ether, deep red Quinone derivative.

A very full discussion of the "Umlagerung" theory is given by Ley (*Jahrb. d. Rad. u. Elek.*, 1909, vi., 341, 381). A short discussion is also given of the theory of indicators, of polymerisation, and of metallic derivatives of organic compounds, especially of cases where the metal is supposed to be present in the inner part of the molecular complex.

ON HYDRAULIC BRONZE.

By SERGIUS KERN, M.E., St. Petersburg.

In order to prepare a good bronze-casting, well keeping water under high pressure, and also steam under the same conditions, take 78 per cent of best copper, 10 per cent of brass, containing 30 per cent of zinc, and 12 per cent of tin.

Melt the copper and the brass in a crucible (capacity not less than 2 cwts.) with a lid; next, add the tin and 1·4 per cent of zinc. Finally, add 0·12 per cent of cupro silicon (10 per cent silicon), and pour the metal int the mould.

This composition in our practice showed very good results.

February 5th, 1911.

Lewis's Medical and Scientific Circulating Library. —The catalogue of new books and new editions that have been added to the library during the last quarter is just to hand; they number about 200, and include many valuable works upon Medicine, Chemistry, and Physics. Included in the list we notice—"The World of Life," by A. R. Wallace; "Induced Cell Reproduction," by H. C. Ross; "Radium, its Physics and Therapeutics," by Dawson Turner; "Inorganic Chemistry," by Sir H. Roscoe and Harden; "Introduction to Physical Chemistry," by J. Walker; and contributions to Physics by Professors J. A. Fleming, J. H. Poynting, and others. The subscription to the library is very reasonable, and books can be sent by post to subscribers, the postage fee being given for each volume. Catalogues and full particulars for membership can be obtained by application to Mr. H. R. Lewis, 136, Gower Street, London, W.C.

ROYAL SOCIETY.

PRESENTATION OF A PORTRAIT OF SIR WILLIAM CROOKES, O.M.

At the rooms of the Royal Society in Burlington House on the 16th inst., a presentation was made to the Society of a portrait of Sir William Crookes, O.M., Foreign Secretary of the Royal Society.

The Portrait, which will be hung in one of the rooms of the Society, was painted by Mr. E. A. Walton, of the Royal Scottish Academy. It has already been exhibited in London (at the Society of Portrait Painters), in Edinburgh, and in the Fitzwilliam Museum at Cambridge. While hanging in the last-named gallery it attracted the attention of certain scientific men, who organised a subscription fund to acquire it for the Royal Society. Professor Meldola and Professor Pope acted as honorary secretaries, and Lord Avebury as honorary treasurer.

A large number of Fellows were present, and a few ladies including Lady Crookes.

The presentation was made on behalf of the subscribers by Professor Meldola, the treasurer (Lord Avebury) being unable to be present.

The President of the Royal Society, Sir Archibald Geikie, in acknowledging the presentation on behalf of the Society, referred to the lustre which Sir William Crookes's researches had shed on British science, and on the Royal Society in particular.

Sir William Crookes, in thanking the subscribers for this distinguished honour—an honour vouchsafed to few living men,—said he valued, even above the award of the Copley Medal in 1904, this appreciation of his scientific work by the many good friends who had subscribed towards this presentation. He alluded to the fact that it was nearly fifty years since the Society had conferred its Fellowship on him. The steadfast encouragement he had received from the Royal Society had often helped to urge him forward in his chosen baffling road of experimental research. He could say from his heart that the cultivation of Science was "its own exceeding great reward," but there was even a greater reward—the esteem and approval of the Fellows of the Royal Society. But, Sir William said in conclusion, the honour and glory of this day belonged not so much to him, but to Mr. Walton, who had not only painted a living likeness, but also had created one of the very best examples of modern portraiture.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 9th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows :—

"*Certain Physical and Physiological Properties of Stovaine and its Homologues.*" By V. H. VELEY, F.R.S., and W. L. SYMES.

The bodies in question comprise the methyl-, amyl-, phenyl-, and benzyl-homologues of stovaine, and in addition a new compound recently prepared by M. Fourneau, viz. :—The propyl ester of dimethyl-amino-oxy-benzoyl-isobutyric acid. The densities of these diminish with increasing molecular weight, and the affinity value of the last-named is less than that already found by the former of us for stovaine and for its methyl homologue.

Fourneau's new compound abolishes the contractility of muscle less rapidly than does stovaine or methyl-stovaine. It has also less effect on blood pressure and on respiration.

Amyl-, phenyl-, and benzyl-stovaine appear to act more slowly on muscle than does stovaine, presumably on account of partial precipitation of their bases. On blood pressure amyl-stovaine has rather more effect than has stovaine.

The pronounced local anæsthetic properties possessed by all these bodies are discussed in the following paper.

"*Effect of some Local Anæsthetics on Nerve.*" By W. L. SYMES and V. H. VELEY, F.R.S.

The bodies dealt with in the preceding paper have been compared with one another, and also with cocaine, as to their effects in blocking the physiological conductivity of frog's nerve.

The anæsthetic block produced by these bodies, when complete for maximal single stimuli (Berne coil at 400 mm.), is also complete for single stimuli many times more intense (Berne coil at 200—100 mm.). A block complete to maximal single stimuli (coil at 400 mm.) is usually also complete to repeated stimuli with the same disposition of the coil. Partial blockage of individual nerve fibres has not been detected.

Stovaine, its homologues, and Fourneau's new salt all block more actively than does cocaine. Stovaine, methyl-stovaine, and Fourneau's new salt block more rapidly than do the remaining bodies. Amyl-, phenyl-, and benzyl-stovaine block more slowly, and the resulting block is less rapidly washed out.

Considered as local anæsthetics, phenyl- and benzyl-stovaine offer no advantage over the remaining bodies. Amyl-stovaine may be of value on account of the relatively long duration of its effect. Methyl-stovaine is the least readily decomposed by faintly alkaline fluids such as lymph and cerebrospinal fluid. Fourneau's new salt has the least effect on circulation and on respiration.

"*Experimental Researches on Vegetable Assimilation and Respiration.* VIII. *A New Method for Estimating Gaseous Exchanges of Submerged Plants.*" By F. F. BLACKMAN, F.R.S., and A. M. SMITH.

The plant is enclosed in a glass chamber, a current of water is kept flowing through the chamber, and samples of the affluent and effluent liquid are analysed at frequent intervals. The alteration in the amount of CO_2 in solution which the liquid undergoes in passing over the plant in the chamber is the measure of the respiration or assimilation that is taking place.

For experiments on assimilation the liquid supplied to the chamber can be enriched with any desired amount of CO_2, and by a special use of a CO_2-generating tower the amount of this gas dissolved can be kept constant for a long period of time. The glass chamber containing the plant is sunk in a large copper water-bath with a glass window, and the temperature and illumination can be controlled.

When the conditions allow vigorous assimilation much oxygen is given off as bubbles from the plant in the chamber, and these bubbles take up an appreciable amount of CO_2 from the solution. It is therefore necessary to collect and measure this gas and use it as a correction to the apparent diminution in the dissolved CO_2. The gas is separated from the liquid by a valve at the highest point of the apparatus, and collected automatically for analysis.

This method has none of the limitations of the bubble-counting procedure exclusively employed previously for the investigation of the assimilation of water-plants, and, since it takes account of the CO_2 in solution and also of that in the gas bubbles, critical measurements can now be made of the assimilation throughout the whole range of the external factors that primarily control this function.

"*Experimental Researches on Vegetable Assimilation and Respiration.* IX. *On Assimilation in Submerged Water-plants and its Relation to Concentration of Carbon Dioxide and other Factors.*" By F. F. BLACKMAN, F.R.S., and A. M. SMITH.

The experiments were carried out by a new method, which takes account of the alteration of the gases in solu-

tion as well as of the gases liberated as bubbles. The aim is to demonstrate the *nature* of the relation between assimilation and the chief environmental factors—CO_2-supply, light-intensity, and temperature. The relation is such that *the magnitude of this function in every combination of these factors is determined by one or other of them acting as a limiting factor*. The identification of the particular limiting factor in any definite case is carried out by applying experimentally the following general principle:—*When the magnitude of a function is limited by one of a set of possible factors, increase of that factor and of that one alone will be found to bring about an increase of the magnitude of the function*. From the data obtained a new type of diagram is constructed, by which it is possible to foretell what value of assimilation in *Elodea* will be attained in any combination of medium magnitudes of the three factors of the environment. In this diagram, against the different values of assimilation as ordinates, are ranged three separate curves showing the degrees of CO_2-supply, temperature, and illumination, which are respectively essential for the attainment of each value of assimilation. For any hypothetical combination of the factors, it follows, by the principle of limiting-factors, that if the three functional values corresponding potentially to these be ascertained from the diagram, then the actual magnitude of assimilation attained with that combination of factors will always be *the smallest of the three potential values*. The last section contains a critical account of the work of previous investigators who interpreted their results on the assumption that there was *a primary optimum* in the relation between assimilation and each external factor. The substantial work of Pantanelli led him to the conclusion that the position of the optimum for any one factor shifts with the magnitude of the other concurrent factors. This can only be a transitional point of view, and from this we have advanced to the standpoint that *the whole conception of optima in this connection is inapplicable*, and breaks down completely on careful analysis. We show in detail that all the experiments of previous workers are more harmoniously interpreted from the point of view of interacting limiting-factors than by the conception of optima.

NOTICES OF BOOKS.

Webster's New International Dictionary, 1911. London: G. Bell and Sons, Ltd.

Except for the "Supplement" of 1900, the last edition of Webster's International Dictionary was published in 1890. The time that has elapsed since then has been a period of unexampled activity in the production of dictionaries and encyclopædias. The proprietors of Webster's Dictionary have not been idle, and the issue of the new edition is the outcome of much labour and a large outlay. The whole work has been practically re-written, and, with a view to facilitating the labour involved in use, many novelties in the arrangement of the matter have been introduced. There are some 400 additional pages and 23,000 fresh words, as well as a large increase of material in the way of fuller definitions, but by the employment of thinner paper and some ingenious space-saving devices the bulk of the book has not been materially increased. One of the most striking of these novelties is the introduction of the "*divided page*." Each page of the vocabulary is set up in two sections, the upper and larger portion containing the most important and familiar words, whilst in the lower section the less familiar and unimportant are given in smaller type; this arrangement, while saving a great deal of space, largely facilitates the use of the book. Generally the work has been brought up to date, and good examples of this are to be found in the words and phrases used in connection with *wireless telegraphy*, *national life and feeling*, and particularly in *medicine*. The editor's aim has been to produce something more than a mere dictionary in the usual acceptance of the word, and many instances are to be found of short illustrated treatises that are both valuable and interesting. Special attention has been given to pronunciation and spelling, and in words of which usage varies the rendering of three American and three English dictionaries are given in addition to that adopted by Webster; recent new forms are distinguished by "Ref. Sp."—"reformed spelling." The separate sections of the old edition assigned to Proper Names, Foreign Phrases and Proverbs, noted Fictitious Persons, and Abbreviations have now all been included in their alphabetical places in the general vocabulary, an innovation that is likely to be found of great convenience. As an instance of the increase in volume of matter embodied in one subject, the words from *leaf* to *leafy* as they appear in the several editions from 1847 to 1911 may be noted; in the first edition the subject occupied some forty lines, in the present nearly four hundred. The pictorial illustrations have been greatly increased in number, and many obsolete ones removed; they now number some six thousand, and, as in the earlier edition, they are reproduced together at the end of the book. A simple but very valuable improvement in the book is the plan that has been adopted of notched edges so that any letter of the alphabet can be instantly turned up. On the whole the editor and staff of specialists are to be congratulated on having concentrated such a fund of information into one volume.

New Reduction Methods in Volumetric Analysis. By Edmund Knecht, Ph.D., M.Sc.Tech., F.I.C., and Eva Hibbert. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1910.

The authors' researches on the use of titanous chloride as a titrating agent are already known to readers of the *Berichte*, in which their methods and the results obtained have been published from time to time, but the reprint of them in the form of a monograph will be none the less welcome to chemists and analysts. The use of titanous chloride in the quantitative analysis of azo dyes and dyestuffs seems likely to be capable of wide application, and colour chemists in particular should not be satisfied till they have tried the method and acquired some facility in it. The monograph gives all the necessary information for the preparation of the titanium solution and its use in the estimation of both metals and non-metals, also of nitro compounds, sugars, &c. A method of determining the degree of mercerisation with its aid is also described. Some volumetric estimations of tungsten and molybdenum in which titanous chloride is not used are included, and a bibliography of the literature on the subject of volumetric analysis by means of $TiCl_3$ is given.

Tests for Coal-tar Colours in Aniline Lakes. By George Zerr. Authorised English Edition by Dr. Charles Mayer. London: Charles Griffin and Co., Ltd. 1910.

The literature on the analysis of aniline lakes is very scanty, and this English translation of Zerr's own treatise on his method of testing for coal-tar colours will be much appreciated by chemists who have to deal with the difficult task of analysing a manufactured lake. Zerr's method is undoubtedly the simplest so far worked out, and has been found quite reliable and complete. In the first part of the book details are given in tabular form of the actions of many reagents and solvents on lakes from coal-tar colours, and the second part contains a complete analytical scheme based upon the solubility in hot water, alcohol, and acetic acid, reactions with sulphuric acid, caustic soda, &c. Finally, not the least valuable part of the book is that in which the author describes experiments in identification performed in the course of his own work, and typical methods of treating an unknown lake are outlined.

A Text-book of Botany and Pharmacognosy. By Henry Kraemer, Ph.B., Ph.D. Fourth Edition. Philadelphia and London: J. B. Lippincott Company.

In the fourth edition of this standard work on pharmacognosy the botanical portion has been thoroughly revised by Dr. Theo. Holm, who has re-written some of the articles. This part gives a complete course of botany for students of pharmacy and pharmacognosy, and is beautifully illustrated. The microanalysis of the important plant constituents is treated in a short new section, which contains photographs of microscopic crystals. The book is the acme of completeness and comprehensiveness, and must be regarded as an invaluable work of reference for pharmacists and drug analysts.

The Manuring of Market-garden Crops. By Bernard Dyer, D.Sc., and F. W. E. Shrivell, F.L.S. New Edition. London: Vinton and Co., Ltd. 1910.

This pamphlet gives a very plainly worded and straightforward account of the advantages to be gained by the systematic use of concentrated fertilisers for manuring market-garden crops. A knowledge of the nature and uses of artificial manures is daily becoming of greater importance to the agriculturist in view of the diminishing production of stable manure, and to the market-gardener, more particularly because he has usually to supply more food for his crops than the general farmer. This book will be found a very good practical guide, giving definite and not too technical instructions as to how to proceed in order to obtain the most satisfactory results. The illustrations show the effects of the use of different manures on many crops; all common garden crops are discussed individually, and practical recommendations as to the best method of treating them are given in detail. The length of time (seventeen years) over which the trials have extended makes the conclusions to be drawn of special value, and in the new edition of the book the record of them has been brought down to the end of the year 1909.

Elektrische Doppelbrechung der Kohlenstoff Verbindungen. ("Electrical Double Refraction of Carbon Compounds"). By Dr. phil. Richard Leiser. Halle-a-S.: Wilhelm Knapp. 1910.

This monograph describes researches carried out from 1907 to 1909 in the Physical and Electrical Chemistry Institute of the Technical High School at Karlsruhe. In the course of the experiments Kerr's constant B was determined for some 150 organic compounds, and the monograph contains a full account of the experimental arrangement adopted and the method of taking the measurements. The results are tabulated, and from a study of the figures the author draws the conclusion that the magnitude of Kerr's constant is closely connected with the chemical constitution, and unlike most other physical properties seems to be considerably influenced by small differences in structure. Various empirical rules have been deduced by which certain conclusions as to the constitution can be drawn from the value of the constant. In conclusion, the author discusses very shortly the theory of the nature of electrical double refraction.

Dizionario di Merceologia e di Chimica Applicata. ("Dictionary of Technology and of Applied Chemistry"). By Prof. Dott. Vittorio Villavecchia. Third Edition. Vol. I. Milan: Ulrico Hoepli. 1911.

Many important additions and alterations have been made in the third edition of this useful dictionary. It gives, besides the Italian, the French, German, English, and Spanish names of a large number of substances used in pharmaceutical and applied chemistry, alimentary products, &c. Under the heading of each substance methods of technical preparation are discussed, its properties are fully described, and its average market price is given. Chemical formulæ are always included where possible, and some account is given of the uses of each substance. The first volume, which includes the letters A to M, appears to fulfil every requirement of accuracy and completeness.

Uber die Erhaltung der Masse bei Chemischen Umsetzungen. ("On the Conservation of Mass in Chemical Transpositions"). By H. Landolt. Berlin: Verlag der Königl Akademie der Wissenschaften. 1910.

The manuscript of this monograph, which was almost ready for press at the time of the author's death, has been revised and slightly altered in places by Prof. W. Marckwald. It gives a detailed description of the author's investigations of the truth of the Principle of the Conservation of Mass, together with some account of the work of other physicists. Full details are given of the methods and apparatus employed, and after a thorough examination into sources of error and corrections to be applied, the final result is stated, viz., that in the fifteen chemical changes studied there is no evidence of any alteration in the total weight of the reacting substances.

Der Kautschuk und seine Prüfung. ("Indiarubber and its Examination"). By Prof. Dr. F. W. Hinrichsen and Dipl. Ing. K. Memmler. Leipzig: S. Hirzel. 1910.

Although the chemistry of rubber is by no means thoroughly elucidated, and there obviously remains much work to be done in investigating its properties and methods of analysis, the advances of recent years have been so rapid and of such importance as to make a summary of the present state of our knowledge well worth preparation. This book is a compilation of all the work published on the subject, and it makes the present position very clear. Such questions of technical importance as the properties of the latex and the physical and chemical properties of raw rubber, and the theory of vulcanisation are very thoroughly treated, and full details are given of methods of chemical analysis, while the mechanical testing is also discussed in a section in which abstracts are given of all the important researches which are now mainly of historical interest as well as of those of quite recent date.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless other ise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 26, December 27, 1910.

Principal Types of Photolysis of Organic Compounds by Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—The photolysis (decomposition by ultra-violet rays) of the primary alcoholic group CH_2OH gives large quantities of hydrogen and some carbon monoxide, but no carbon dioxide. In fatty alcohols of the type RCH_2OH the gaseous hydrocarbons R_2 are also formed. Primary alcohols with a branching chain, $R.R':CH.CH_2OH$, do not give the hydrocarbons R_2 or $R.R'$, but their side chains break more easily, and methane and ethane are formed. With allylic alcohol the same result is obtained. The primary aldehyde group, COH, gives some carbon monoxide and hydrogen and a small quantity of CO_2, while the secondary aldehydes give carbon monoxide and no hydrogen. The decomposition of ordinary acetone is shown by the equation

$CH_3.CO.CH_3 = CO + C_2H_6$. The acid group CO_2H gives chiefly carbon dioxide, some hydrogen, and carbon monoxide.

Brown Gold..—M. Hanriot.—When an alloy of gold and silver (containing one-fifth of gold) is attacked by nitric acid the silver dissolves, and the gold is left in a spongy brown mass, to which the author has given the name "brown gold." When it is washed with water till it is neutral it still retains some nitric acid, which it loses at 175—200°. If heating is continued it changes colour and contracts; at 900° gases are evolved, and it fuses at 1040° and then acquires the properties of ordinary gold. The amount of contraction varies with the composition of the original alloy, being greater the higher the percentage of silver.

Action of Ether-salts on the Monosodium Derivative of Benzyl Cyanide.—F. Bodroux.—The ether salts of aromatic monobasic acids and of dibasic fatty acids react with the monosodium derivative of benzyl cyanide, giving compounds of formula—

$$C_6H_5—CH(CO.R)—CN$$

Thus ethyl benzoate gives phenylcyanacetophenone. Ethyl carbonate gives ethyl phenylcyanacetate, but ethyl oxalate gives Erlenmeyer's ethyl phenylcyanopyruvate.

Condensation of Acrolein Bromide with Malonic Acid.—M. Lespieau.—In acetic acid solution acrolein bromide reacts with malonic acid, giving a saturated acid of formula $CH_2Br—CHBr—CHBr—CH_2—CO_2H$. Tribromovaleric acid is very readily decomposed by potash, giving hydrobromic acid, and may be etherified by alcohol in presence of hydrochloric acid. With zinc and alcohol it yields the pentenic acid $CH_3—CH=CH—CH_2—CO_2H$.

Complex Salts of some Amino Acids. — L. Tchougaeff and E. Serbin.—Chromic salts of amino acids can be very readily prepared by allowing excess of the acid to react with purpureo-chromic chloride, $[Cr_5NH_3Cl]Cl_2$, in presence of water at 100°. The chromic derivative of glycine, $Cr(CH_2NH_2CO_2)_3$, is a stable red crystalline substance only very slightly soluble in water and in the usual organic solvents. The asparagine derivative is even loss soluble. The same chromic compounds can be obtained by boiling the α-amino-acids with green chromic chloride, $CrCl_3.6H_2O$, containing ammonia.

Preparation of Aromatic Acylguanidines. — P. Pierron.—The reaction—

$$R_1—CO—NH—CN + HCl.NH_2—R_2 = R—CO—NH—C(=NH)—NH—R_2.HCl$$

takes place quantitatively if the reagents are boiled together in alcoholic solution for some hours. Thus benzoyl cyanamide and aniline chlorhydrate give benzoylphenylguanidine chlorhydrate. The free base can be separated by saturating the hot aqueous solution with potash. It is decomposed by boiling with caustic soda, yielding phenyl-guanidine.

Glucodeconic Acids.—L. H. Philippe.—When a solution of β-glucodeconic acid is evaporated a mixture of two substances is obtained—the lactone hydrate, $C_{10}H_{18}O_{10}H_2O$, and the acid anhydride, $C_{20}H_{38}O_{21}$. They can readily be separated by means of boiling alcohol, in which the anhydride is insoluble. The lactone and anhydride in hot aqueous solution are slowly transformed into one another. The α- and β-lactones can be separated either by fractional crystallisation in water and dilute alcohol, or more simply by the difference of solubility of their phenylhydrazides.

Zeitschrift fur Anorganische Chemie.
Vol. lxix., No. 2, 1911.

Accurate Determination of Sulphur in Pyrites and Marcasite.—E. T. Allen and John Johnston.—When sulphides of iron are ground up for analysis partial oxidation takes place, with formation of sulphur dioxide and ferrous sulphate, and if the material is finely powdered the error cannot be neglected; it may be reduced to 0·05 per cent by careful grinding till the material will pass through an 8 (per cm.) mesh sieve. When material which is not uniform has to be powdered, the error can be determined by washing out a weighed amount of the powder with boiling water in an atmosphere of carbon dioxide and determining the iron in the washings. The authors find that there is no loss of sulphur in Carius's method (oxidation in closed tubes), but Lunge's and Fresenius's methods both give low results owing to loss of sulphur by oxidation. In an improved method the iron is removed by two precipitations with sodium carbonate. In the precipitation of barium sulphate the free acid must be limited to a small definite amount, and precipitation must be effected at a definite rate. Three corrections must be applied to the weight of the barium sulphate precipitate—(1) A correction for solubility, depending on the volume of the solution and the amount of free acid; (2) a correction for the occlusion of sodium sulphate in the precipitate, which depends on various circumstances, but chiefly upon the amount of alkali chloride originally present in the solution; (3) a correction for the free sulphuric acid set free on heating.

Behaviour of Metaboric and Metaphosphoric Acids in the Melts of their Alkali Salts.—H. S. van Klooster.—In the system $KPO_3—KBO_2$ the melting-point curve indicates the formation of a compound, $KPO_3.KBO_2$. This compound is the salt of a complex acid which also exists in aqueous solution. In melts of sodium metaphosphate and sodium borate a compound is probably formed, but its composition could not be accurately determined by thermic methods. Probably its formula is $NaPO_3.NaBO_2$. The melting-point diagram of mixtures of $NaBO_2$ and KBO_2 is a characteristic mixed crystals diagram. In the system $LiBO_2—NaBO_2$ the composition of the eutectic is 50 per cent $LiBO_2$. The miscibility in the crystalline state is very small.

Binary Systems: $Li_2O—SiO_2$, $Li_2SiO_3—ZnSiO_3$, $ZnSiO_3—CdSiO_3$, $Li_2SiO_3—LiBO_2$, $Na_2SiO_3—NaBO_2$, and $Na_2SiO_3—NaWO_4$.—H. S. van Klooster.—In the binary system $Li_2O—SiO_2$ only two compounds exist, the ortho and metasilicates of lithium; in the crystalline condition they are only slightly miscible, but Li_2SiO_3 can take up isomorphously up to 24·3 per cent of SiO_2. In the system $ZnSiO_3—CdSiO_3$ an isomorphous series of mixtures with a minimum at 25 per cent $ZnSiO_3$ was detected by the thermic method, but this observation could not be completely confirmed optically. Na_2WO_4 at temperatures below 1100° is only very slightly miscible in the fluid state with Na_2SiO_3, or else not at all. There is no miscibility in the crystalline state. The data for the other systems are given in the following table:—

Binary system.	Miscibility in cryst. state (per cent).	Eutect. cryst. in weight per cent.	Temp. of eutect. cryst.
$Li_2SiO_3—ZnSiO_3$.	71 (?)—7 (?) Li_2SiO_3	52 (?) Li_2SiO_3	990 (?)
$Li_2SiO_3—LiBO_2$ ..	91—24 Li_2SiO_3	22 Li_2SiO_3	803
$Na_2SiO_3—NaBO_2$.	96—5 Na_2SiO_3	55 Na_2SiO_3	815

It is clear from this table that the components are only slightly miscible in the solid state.

Salts of a Green and a Violet Propionato-chromium Base.—R. F. Weinland and Karl Hoehn.—The authors have prepared a sesquichromate, a chloride-chromate, and a monopropionate of a hexapropionatotrichromic base. This green base is completely analogous to the green hexa-acetato base. A new type of compounds, the salts

of a violet propionato base, have now been prepared. When an aqueous solution of the monopropionate of the green base is evaporated, a violet oily liquid separates, and from it violet crystals can be obtained. Moreover, freshly precipitated chromic hydroxide dissolves in cold propionic acid, giving a violet solution. The violet crystals are the dipropionate of the pentapropionatotrichromic base—

$$\left[Cr_3 \begin{matrix}(C_2H_5COO)_5\\(OH)_2\\(H_2O)_2\end{matrix}\right](C_2H_5COO)_2.$$

The green base is transformed into the violet base by the elimination of a propionic acid residue from the cation :—

$$\left[Cr_3 \underset{\text{Green.}}{\begin{matrix}(C_2H_5COO)_6\\(OH)_2\end{matrix}}\right]C_2H_5COO + H_2O \rightleftharpoons$$

$$\rightleftharpoons \left[Cr_3 \underset{\text{Violet.}}{\begin{matrix}(C_2H_5COO)_5\\(OH)_3\end{matrix}}\right]C_2H_5COO + C_2H_5COOH.$$

The reverse process can also be effected. All the salts of the violet base which have been prepared are very soluble in ether and chloroform, while the salts of the green base are insoluble in ether. The dipropionate of the violet pentapropionato base is isomeric with the monopropionate of the green hexapropionato base. On the addition of sodium propionate to a solution of green chromic chloride hydrate a violet chromic propionate separates.

Catalysis by Chromic Acid and its Salts.—Eugen Spitalsky.—A very accurate method of analysing very dilute solutions of chromic acid can be based upon a combination of Györy's method with the reaction between arsenious acid and chromic acid. By means of this method it may be shown that the amount of chromic acid reduced in reacting with hydrogen peroxide increases with the concentration, till at about 0·2 mol. H_2O_2 to 0·00543 mol. CrO_3 it reaches its limiting amount (28·3 per cent), after which it does not change. A chromic acid solution in which more than 28·3 per cent of its chromium was reduced to chromium oxide is again oxidised by H_2O_2, and as the initial concentration of the H_2O_2 increases the oxidation gradually increases until exactly the same limiting proportion (28·3 per cent) is reached. In the re-oxidation of the chromic mixture the amount of oxidation is increased if quantities of H_2O_2 which are insufficient to reach the limiting proportion are allowed to act twice after one another. When the limiting amount is once reached it is not altered by the repeated action of larger quantities of hydrogen peroxide. The course of the catalytic reaction is quite independent of the initial state of the catalyser, and chromic acid may be regarded as an ideal catalyser for hydrogen peroxide.

MISCELLANEOUS.

South-Western Polytechnic Institute, Chelsea.—Sir Alfred Keogh, K.C.B., LL.D., Rector of the Imperial College of Science and Technology, presents prizes and certificates to students of Evening Classes and Day College on March 10th, at 8 o'clock p.m. Laboratories and workshops open to public inspection at 9.15 p.m.

International Chemical Engineering and Industries Exhibition.—From information which we have received there is every indication that the Chemical Engineering and Industries Exhibition to be held at the Royal Agricultural Hall in May next will be a success. The undertaking has certainly provoked an amount of interest not usually evinced in Exhibitions, for not only does the Hon. Advisory Council embrace the President, ex-Presidents, and many of the Officers and Members of the Society of Chemical Industry, but strong and influential Committees are at work in Manchester, Liverpool, Glasgow, Newcastle, Leeds, Sheffield, Birmingham, and other commercial centres, the desire being that chemical engineering in its various branches may be thoroughly represented. Although Engineering Exhibitions of a general character have been held, this is the first attempt which has been made to bring together appliances and apparatus specially designed for, or in use in, chemical works. The following list of exhibits which it is proposed to include will better indicate the character and scope of the Exhibition :—Acetylene plants; acid-proof apparatus, ware, pipes, &c.; acid-proof valves and fittings; air compressors; blowers and exhausters; box making machinery; bricks, tiles (fire and acid-proof); casks, drums, carboys, stone and glass ware; conveyors, elevators, ropeways, hoists, and lifting tackle; distilling, evaporating, and drying apparatus; dust removing and dust collecting plant; electrical appliances; electric driving plant; engines and boilers; engineering accessories; extraction and recovery plant; fans; filtering apparatus; fire appliances; forced and induced draught appliances; fuel economisers, mechanical stokers; furnaces and furnace fittings; grinding and crushing machinery; health protecting, safety, and first aid appliances; hydro-extractors; laboratory, scientific, and optical apparatus; lighting, heating, and ventilating appliances; mixing, sifting, stirring, filling, and packing machinery; pharmaceutical machinery; portable railway and rolling stock; presses (hydraulic); pumps; refrigerating and cooling plants; roofing (gas, fume, and acid-proof); separation machinery for clay and mineral compounds; shop tools; smoke preventing apparatus; stills and vacuum pans; stoneware chemical apparatus; suction gas plant; tanks and cisterns; tubes, coils, and fittings; water softening and purification plants; wagons, trucks, tubs, and corves; weighing machinery; welding and cutting plants.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Royal Society of Arts, 8. (Cantor Lecture). "Brewing and Modern Science," by Prof. A. J. Brown.

TUESDAY, 28th.—Royal Institution, 3. "Crystalline Structure—Mineral, Chemical, and Liquid," by A. E. H. Tutton.

—— Royal Society of Arts, 4.30. "The Resources and Problems of the Union of South Africa," by The Hon. Sir Richard Solomon, K.C.B.

WEDNESDAY, March 1st.—Society of Public Analysts, 8. "Examination of the Process of Shrewsbury and Knapp for the Estimation of Cocoanut Oil," by R. Ross, J. Race, and F. Maudsley. "Estimation of Iron by Permanganate in presence of Hydrochloric Acid," by A. C. Cumming and A. Gemmell. "Analysis of Sweetened Condensed Milk," by A. Backe. "Note on Henry C. Frey's Method of Estimating Petroleum in Turpentine," by H. S. Shrewsbury. "Formation of Hypoiodites, and their Action on Sodium Thiosulphate—a Source of Error in certain Iodine Titrations," by J. P. Batey. A New Form of Specific Gravity Apparatus will be shown by Dr. C. B. Savory.

—— Royal Society of Arts, 8. "Caisson Sickness and Compressed Air," by Dr. Leonard Hill, F.R.S.

THURSDAY, 2nd.—Royal Institution, 3. "Ruskin," by A. C. Benson.

—— Royal Society. "Reversal of the Reflex Effect of an Afferent Nerve by Altering the Character of the Electrical Stimulus applied," by Prof. C. S. Sherrington and Miss S. C. Sowton. "Carbon Dioxide Output during Decerebrate Rigidity," by Dr. H. E. Roaf. "Alcoholic Ferment of Yeast Juice—Part VI., Influence of Arsenates and Arsenites on the Fermentation of the Sugars by Yeast Juice," by Dr. A. Harden and W. J. Young. "Experiments to ascertain if certain *Tabanidæ* act as the Carriers of *Trypanosoma pecorum*," by Col. Sir D. Bruce and others.

—— Chemical, 8.30. "Potassium Cupricarbonates," by by S. U. Pickering. "Studies in the Camphane Series—Part XXIX, A New Phenylhydrazone of Camphorquinone," by M. O. Forster and A. Zimmerli. "Synthesis of Dipeptides of Lauric Acid with Glycine, Alanine, Valine, Leucine, and Asparagine," by A. Hopwood and C. Weizmann. "Fluorone Derivatives," by F. G. Pope and H. Howard. "Constituents of *Withania somnifera*," by F. B. Power and A. H. Salway.

FRIDAY 3rd.—Royal Institution, 9. "Scents of Butterflies," by F. A. Dixey.

SATURDAY, 5th.—Royal Institution, 3. "Radiant Energy and Matter," by Prof Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. CIII., No. 2675.

STUDIES OF THE PROCESSES OPERATIVE IN SOLUTIONS.*

XIX.—The Complexity of the Phenomena afforded by Solutions: a Retrospect.

With an Addendum on Non-aqueous Electrolytes.

By HENRY E. ARMSTRONG.

In presenting this series of communications to the Society on the processes operative in solutions (XII—XVIII), a subject that has occupied my thoughts during many years past, I may be permitted to offer a summary of previous parts and to explain briefly the views that are advocated.

In discussing the conditions determinative of chemical change in the Presidential Address to the Chemical Section of the British Association at Aberdeen, in 1885, I was led to consider somewhat fully the nature of the operations involved in electrolysis and to take exception to the view advocated by F. Kohlrausch that the solvent plays a merely mechanical part in the process. This course was adopted because, earlier in the year, in discussing Brereton Baker's communication to this Society on "Combustion in Dried Gases" (*Proc.*, 1885, i., 37), I had given a definition involving the assumption that, in all cases, *a chemical change is essentially an electrolytic process*; on this account, I have always contended that the presence of an electrolyte is necessary to the occurrence of change: that change only takes place when a conducting system is established—a system consisting of three distinct components, one of which is an electrolyte.

I venture to claim that, in the course of years, this prevision has been fully substantiated: the evidence is now overwhelming that two pure substances cannot interact; a third component must be present to bind them into a conducting system. No argument from kinetic premises that the chance of a meeting taking place of three, let alone of four, dissimilar molecules is infinitely small can prevail against the fact that apparently the necessary number do find a means of meeting when occasion requires. My contention is one of fundamental importance: if correct, we must regard with some doubt the general accuracy of the interpretations now given of the electric discharge in highly exhausted vessels—we must, in fact, ask for further evidence in proof of the conclusion that the so-called negative electrons are finer material than hydrogen atoms and that the large positive electrons are otherwise than congeries of ordinary atoms such as would remain if the systems referred to above were electrolysed in the path of a discharge. The argument on which the determination of the size of the electron has been based is certainly one that is open to question. In the discussion that took place recently at Sheffield before the Chemical and Physical Sections of the British Association, I referred to the proof given by Sir James Dewar that if the atmosphere of a tube containing helium be "purified" to the highest possible extent by means of charcoal cooled in liquid hydrogen, it is impossible to urge an electric discharge across the tube, although the vanes of a radiometer mounted within the tube rotate merrily under the influence of heat rays. When I spoke of this as proof that the occurrence of a discharge is dependent on the presence of some conducting impurity in the atmosphere—on the presence of an electrolyte—Sir Joseph Thomson asked, "What is an electrolyte?" He seemed to imply that no distinction was to be drawn between electrolytes and non-electrolytes—that whether a compound behaved as an electrolyte or not was merely a question of the intensity of the electromotive force applied. The incident is of interest, if only as showing that no agreement has yet been arrived at on an issue of extraordinary importance in both chemical and physical science. Most chemists probably are satisfied with Hittorf's definition, "Electrolytes are salts." When discharges are caused to take place by high electromotive forces, it is perhaps because disruptive effects are produced—because buried "impurities" are brought into action.

It is remarkable that no clear conceptions as to the nature of the process of chemical change have yet taken possession of the field; it is more than surprising that no proper discussion of the interactions of metals and acids is to be found in the text-books, that we should still hear actions spoken of as partly chemical, partly electrical, as if it were possible to draw a distinction—this too while all apparently are prepared to agree that the force we speak of as chemical affinity is electrical in its origin. The introduction of the electrolytic dissociation hypothesis seems to have retarded rather than advanced progress by substituting a pretentious terminology for ordinary simple language. The lack of outlook is particularly noticeable when the perennial discussion on the rusting of iron breaks out afresh—the amount of labour spent to no purpose in the attempts to settle this problem would have been far less had any clear conception been formed of the conditions determinative of chemical change in general.

In 1886 my views on electrolysis were more fully stated in a communication to the Royal Society which bore the significant title "Electrolytic Conduction in Relation to Molecular Composition, Valency and the Nature of Chemical Change, being an Attempt to Apply a Theory of Residual Affinity" (*Proc. Roy. Soc.*, 1886, xl., 268).

In this essay, exception was taken very definitely to the hypothesis advocated by Clausius, in 1857, that a certain small proportion of the molecules in a conducting solution are *kinetically* broken up into their constituent atoms. This was at a time when the radical extension of this hypothesis advocated with such remarkable ability by Arrhenius (1883) was scarcely known to chemists and before I had been able to procure his memoir. I also contended that the Helmholtz atomic charge hypothesis was not in accordance with the facts as these were known to chemists and specially drew attention to the unsaturated character of water and to the need of taking "residual affinity" into account in interpreting chemical phenomena."

The contentions advocated in the Address referred to and in my communication to the Royal Society were maintained by me in the Reports of the British Association Committee on Electrolysis up to 1889. I received most valuable support from Professor Fitzgerald, especially at the Leeds meeting in 1890.* The Helmholtz Memorial Lecture contributed to our Society by this physicist in 1896 may be referred to here as a very noteworthy contribution to the discussion of the phenomena afforded by solutions which has been conveniently overlooked by many.

I have gone so far, in years past, as to contend that the hypothesis of electrolytic dissociation is an offence against chemical common sense and in no way a necessary assumption. I am still of this opinion. The great advance that has been made in the course of the dis-

* This communication, most unfortunately, was submitted with others to the Society for the Propagation of Christian Names among Chemists. I have withdrawn it and others to which my name is attached as a protest against the refusal of the Publication Committee of the Society to grant me the liberty which, in the interests of scientific progress, I contend must be allowed to every author of a scientific communication—that of expressing himself in the terms chosen by himself. The previous communications of the series (I.—XI.) have been published in the *Proceedings of the Royal Society*—the one Society that unites the interests of all branches of experimental inquiry. I have asked nothing more than that I may not be prevented from using the language I have used in these previous communications—language which I used of set purpose. I am the more annoyed to be obliged to take this course as I unwillingly interrupted my series of communications to the Royal Society to meet the wishes of certain friends, who represented that our work was practically withheld from the notice of chemists when published by that Society. My experience, however, is only another proof among the many that are daily set before us that any attempt to practice altruism is a mistake.—Henry E. Armstrong.

* Report of the British Association, p. 142.

cussion is the general recognition of the fact, already perceived by not a few of the early workers from Berthollet onwards, that of the total mass of a substance in solution only a certain proportion is active at any given moment; it is this activated part that many are pleased to regard as 'electrolytically dissociated.' The problem before us is the determination of the nature of the process of "activation."

One great disadvantage of the electrolytic dissociation hypothesis, apart from all other considerations, is that it is only applicable to electrolytes; an association hypothesis, such as I have advocated, is generally applicable. In discussing the laws which govern substitution in the benzene series in 1887 (*Trans.*, lxi., 261), I drew attention, in fact, to Kekulè's representation of the substitution process as involving initially the association of the interacting molecules and advocated the general adoption of this view.

In the Presidential Address to the Society on the "Nature of Chemical Change," delivered in 1895 (*Trans.*, lxvii., 1122), in which I summarised my views on the subject, particular attention was drawn to the importance of considering the changes effected by the agency of enzymes, as these act selectively. I have since had the opportunity of studying such changes in detail; the results arrived at, described in a series of communications to the Royal Society from my laboratory, are uniformly in favour of an association hypothesis; in fact, it seems to be impossible to interpret the changes induced by enzymes from the point of view of a dissociation hypothesis.

The study of enzymes led me to take up that of hydrolytic agents generally, whether alone or in presence of other substances, in the hope of arriving at an understanding of the processes operative in solutions.*

I contended in 1886 that the increase in molecular conductivity observed on diluting aqueous solutions was the consequence of "the specific influence of the fundamental molecule of the compound (the solute) making itself more and more felt as by dilution it becomes more and more disentangled from its fellows." I contended, also, that electrolysis was a "reciprocal process" in which both solute and solvent were concerned; in fact, I went so far as to conclude "that there is no satisfactory evidence that the constituents of the electrolyte are either free prior to the action of the electromotive force or are primarily set free by the effect produced by the electromotive force upon either member *separately* of the *composite* electrolyte; but that an additional influence comes into play, namely, that of one member of the composite electrolyte upon the other while both are under the influence of the electromotive force. This influence, I imagine, is exerted by the negative radicle of the one member of the composite electrolyte upon the negative radicle of the other member." In another section of the paper, this influence was attributed to the residual affinity exhibited more especially by negative elements. Particular stress was laid on the contention that the properties of water could not be explained except on the assumption that the fundamental molecule represented by the formula OH_2 was "eminently unsaturated," the implication being, of course, that water itself was to be regarded as consisting of complex molecules or molecular aggregates.

It was not until 1900 that I saw my way to a more complete explanation of the phenomena presented by aqueous solutions. The conclusions arrived at were practically stated in the article "Chemistry" in Vol. 26 of the *Encyclopædia Britannica* (p. 741) published in 1902. They were more fully presented in a communication to the Royal Society in June, 1906, on the "Origin of Osmotic Effects" and in Part VI. of these studies published in 1908 (compare *Science Progress*, Nos. 11 and 12, January and April, 1909).

I have never been able to accept the kinetic explanation of so-called osmotic pressure put forward by van 't Hoff, having felt that the phenomena are to be regarded as in some way the outcome of attractions exerted within the liquid. The character of these attractive influences was not easily perceived; it is always difficult to overcome the force of preconceived ideas. The view which I have been led to take cannot be more succinctly stated than in the words used in my paper of 1906 (p. 265):—

"The effect of introducing neutral molecules—non-electrolytes—into liquid water must be to cause the dissociation of the molecular complexes to an extent corresponding to the proportion in which the neutral molecules are added. If a substance enter into solution entirely in the form of its fundamental molecules, it will produce its normal effect, provided that its own attractive effect upon the water molecules be inappreciable.

"Electrolytes, besides producing the dissociating effect, must be supposed also to exercise an attractive effect on water molecules. In ordinary water, the state of equilibrium involves the simple dissociative change pictured in the equation—

$$(H_2O)_n \rightleftharpoons nH_2O$$

in which n may have several values, as probably there is a greater number of forms present than two. The introduction of any substance into solution involves the disturbance of the equilibrium in the direction $(H_2O)_n \rightarrow nH_2O$. The osmotic 'pressure' is the measure of the extent to which equilibrium is thus disturbed by the liberation of the fundamental molecules or *monads*. These monads are to be regarded as the attractive element in the region of the solution and as conditioning a flow of similar molecules from the region of the pure solvent—or from a more dilute solution—until the two regions are in equilibrium.

When this explanation occurred to me, it was obvious that the prevailing method of contrasting substances in solutions made up to certain volume strengths must furnish inconclusive results: in other words, in comparing the osmotic efficiency of substances, it is essential to measure their influence on one and the same proportion of solvent.

In the case of solutions, mass of solvent – not the volume of the solution—plays a part comparable with that played by volume in the case of gases. It was from this point of view that R. J. Caldwell, at my request, undertook the investigation described in the first of these studies on the influence of salts on the hydrolytic activity of acids. At about the same time, for reasons which are by no means clear, Morse and Frazer made use of a similar method of treatment in their refined studies of osmotic pressure. R. J. Caldwell was able to show that the anomalies presented by concentrated in comparison with dilute solutions when volume-normal solutions are contrasted for the most part disappear when weight-normal solutions are used. In the present series of communications, a further step is taken in that the attempt is made to arrive at a determination of the amount of controlled water present in a solution; it is obvious that valid comparisons are only to be made between solutions containing equal amounts of water in the same state—of water in no way combined

* Studies of the Processes Operative in Solutions. Parts I.—XI.

I.—"The Sucroclastic Action of Acids as influenced by Salts and Non-Electrolytes." By R. J. Caldwell (*Proc. Roy. Soc.*, 1906, lxxviii., A, 272).

II.—"The Displacement of Chlorides from Solution by Alcohol and by Hydrogen Chloride." With J. V. Eyre, A. V. Hussey, and W. P. Paddison ([Parts II.—V.], *Proc. Roy. Soc.*, 1907, lxxix., A, 566)

III.—"The Sucroclastic Action of Nitric Acid as influenced by Nitrates." By R. Whymper.

IV.—"The Hydrolysis of Methylic Acetate in Presence of Salts." With J. A. Watson.

V.—"The Discrimination of Hydrates in Solution." With R. J. Caldwell.

VI.—"Hydrolysis, Hydrolation and Hydronation as Determinants of the Properties of Aqueous Solutions." ([Parts VI.—X.], *Proc. Roy. Soc.*, 1908, lxxxi., A, 8).

VII.—"The Relative Efficiencies of Acids as deduced from their Conductivities and Hydrolytic Activities." With E. Wheeler."

VIII.—"The Influence of Salts on Hydrolysis and the Determination of Hydration Values." With D. Crothers.

IX.—"The Determination of Optical Rotatory Power." By R. J. Caldwell and R. Whymper.

X.—"The Changes effected by the Reciprocal Interference of Cane-Sugar and other Substances (Salts and Non-electrolytes) in Aqueous Solutions." By R. J. Caldwell and R. Whymper.

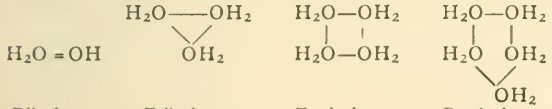
XI.—"The Displacement of Salts from Solution by various Precipitants." With J. V. Eyre (*Proc. Roy. Soc.*, 1910, lxxxiv., A, 123).

with or controlled by the solute. It is doubtful if it will be possible ever to estimate this, as every variation in the behaviour of a solute in presence of a solvent must exercise a corresponding influence on the whole mass of solvent in which it is distributed. Solutions of two different substances ostensibly of the same concentration would contain like amounts of free water only if the two substances behaved alike towards water; any difference in the composition or character of their hydrates would throw them out of step.

If we are studying the alterations in water produced by this or that substance—the alterations in its boiling or freezing-point, for example—the simplest logic would seem to indicate that it is essential to make comparison of the effects produced in one and the same quantity of water, not to allow this to vary from experiment to experiment as it does when volume normal solutions are used.

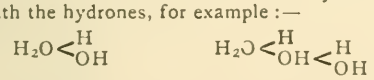
To secure precision and avoid confusion, it will be advisable in future to retain the name water for the liquid and to give a distinct name to the simple molecule represented by the symbol OH_2; only in this way will justice be done to the marvellous properties of water. I have suggested that the fundamental molecule of water be called *Hydrone*, in recognition of its ketonic character.

It is scarcely probable that we shall be able ever to determine the precise nature of the components of water; at present we certainly cannot do otherwise than use the argument from analogy. The suggestions I have made are based on the assumption that, in so far as it acts as a tetrad element, oxygen may be compared with carbon, the chief difference being that the unions contracted by the oxygen unit OH_2 are far less firm and lasting than those contracted by the corresponding carbon unit CH_2; consequently, a series of polyhydrones are conceivable corresponding in structure to the polymethylenes, namely:—



Dihydrone. Trihydrone. Tetrhydrone. Penthydrone.

It is conceivable also that hydrone may give rise by polymerisation to a series of *ols* of the ethylidene type isomeric with the hydrones, for example:—



Hydronol. Dihydronol.

Water, under all conditions, must be saturated with hydrone; the amount of this constituent must be larger the higher the temperature. At low temperatures, water must contain a certain proportion of ice-molecules in solution. Ice, to judge from its viscous character, probably contains a not inconsiderable amount of some form of liquid water molecule and only becomes a definite substance when its temperature is lowered considerably; there are no data apparently from which it is possible even to approximate to a value for the degree of polymerisation reached in ice—to regard it as trihydrone would be altogether premature.

On account of the extreme volatillty of the lower polymethylenes, taking also into account the rise in boiling-point as they increase in molecular weight, the high boiling-point of water may be taken as an indication that the higher, rather than the lower, polyhydrones are its principal constituents. Moreover, on the assumption that oxygen simulates carbon, the affinities of the two atoms are to be regarded as similarly directed—penthydrone is therefore presumably a more stable compound than any of the lower hydrones, just as pentamethylene is more stable than its lower homologues; the boiling-point of such a compound might well be predicted to be about that of water. The fixity of water in comparison with other simple hydrides with which it is usually compared is certainly very remarkable; some special explanation is required to account for the low degree of volatility by which it is characterised. In the absence of all definite proof, arguments such as these have their value, although in no way conclusive; the conclusion to which they point that water is probably rich in penthydrone is certainly not irrational.

It is to be supposed that when substances are dissolved in water, various "hydrates" are formed, the which hydrates correspond more or less closely with the hydrols and hydrones comprised in water; the manner in which "hydration" takes place will depend not only on the nature of the substance dissolved but also on the concentration and the temperature. The water must also undergo constitutional changes, owing to the dissociating influence exercised by the molecules of the solute on the various aggregates normally present in the liquid; presumably, the changes will be at a maximum in concentrated solutions.

(To be continued).

THE

DENSITY OF NITON ("RADIUM EMANATION"), AND THE DISINTEGRATION THEORY.*

By Dr. R. WHYTLAW GRAY and Sir WILLIAM RAMSAY, K.C.B., F.R.S., University College, London.

(Concluded from p. 88).

Before proceeding to cite the experimental results, we have still to explain how the exact volume of niton weighed was ascertained. Taking as a basis our previous measurements, which proved the equilibrium amount of niton yielded by the total amount of radium at our disposal to be 0·127 cub. mm. at normal temperature and pressure, we had to determine what fraction of this amount was actually present in our weighing-tube. This was conveniently done by measurement of the γ-ray activity by help of a small aluminium electroscope. The procedure was as follows:—

The emanation was drawn off from the radium-bulbs at definite intervals of time, usually eight or nine days. After explosion of the mixed oxygen and hydrogen gases, it was allowed to stand for several hours, so that the quick-change products should accumulate, and its γ-ray activity was measured in the usual way. It was next introduced into the density-tube, and frozen there, as described for xenon, and the hydrogen was removed by pumping; about 10 per cent of the niton was pumped off with the hydrogen, for the niton has some vapour-pressure at $-195°$. The γ-ray activity of the gas removed was compared with that in the sealed-off density-tube, after a suitable interval of time. Other measurements were made to determine the quantity remaining in the purifying apparatus; but in most cases this was negligible, and, as a rule, the radio-activity of the pumped-off gas, plus the radio-activity of the gas in the weighing-tube, were together equal, after corrections for the decay had been made, to the initial total radio-activity of the gas before it had been purified. It was found, however, that some niton had entered the walls of the weighing-tube; this fraction was estimated by determining the radio-activity of the empty tube, immediately after it had been weighed. Obviously, this emanation had not been removed by the pump. In the table which follows, this amount appears in the column "volume left in tube"; it has been subtracted from the total volume.

The operations of drawing and purifying the emanation, measuring its radio-activity, counterpoising and weighing the density-bulb, and measuring the radio-activity of the amount pumped off, as well as that in the weighing tube, required a long day, so that the density-tube could not be broken until twenty-four hours after the niton was drawn; the actual volume of niton present at the moment of

* A Paper read before the Roya Society, January 12, 1911.

Table of Results.

No. of expt.	Time of accumulation.	Total volume of niton.	Volume pumped off.	Decay of niton.	Volume left in tube.	Volume weighed.	Apparent weight.	Weight of air replacing niton.	Correction for displacement due to glass and air.	Correction for weight of helium produced from niton.	True weight of niton.	Atomic weight of niton.
	Days.	Cub. mm.	Cub. mm.	Cub. mm.	Cub. mm.	Cub. mm.	Micro-mgrm.	Micro-mgrm.	Micro-mgrm.	Micro-mgrm.	Micro-mgrm.	
1.	8	0·0969	0·0052	0·0182	0·0007	0·0728	721	+31	−29+24	−8	739	227
2.	9	0·1017	0·0188	0·0163	0·0100	0·0566	477	+103	−16+15	−7	572	226
3.	9	0·1017	0·0135	0·0253	0·0039	0·0590	577	+37	−22+9	−10	591	225
4	8	0·0969	0·0119	0·0157	0·0016	0·0677	673	+10	−26+12	−6	663	220
5.	8	0·0969	0·0082	0·0152	0·0005	0·0730	704	+29	−33+16	−6	710	218
										Mean		223

A complete reproduction of Experiment 5 may be given, to show how all the requisite data are obtained and utilised.

Volume of niton accumulated in eight days = equilibrium quantity × fraction surviving .. 0·127 × 0·763 = 0·0969 cub. mm.
γ-ray activity of this sample, divisions per hour . .. . 3996 divisions
γ-ray activity of fraction pumped off 353 ,,
Hence amount pumped off .. .. 0·0082 cub. mm.
Amount of niton in weighing-tube = 0·0969 - 0·0082 = ... 0·0887 ,,

The weighing-tube was then counterpoised on the balance.

Pressure in balance-case .. .. .. 54·4 mm.
Zero on scale of beam of light reflected from mirror . .. . 155 ,,

Twenty-five hours after drawing, the weighing-tube was broken.

The gas pumped out, however, was not the original 0·0887 cub. mm., but that volume multiplied by the decay-factor for twenty-five hours, 0·828, viz. .. .. 0·07347 cub. mm.
Pressure in balance-case after breaking the density-tube .. .. 34·7 mm.
Pressure-change = 54·4 - 34·7 . .. 19·7 ,,
Zero on scale after breaking .. .. 154 ,,
Difference of zero = 155 - 154 = 1 mm. But from measurement, 10 mm. pressure = 77 scale divisions; hence 1 division = 10/77 = .. 0·13 ,,
This must be added to the pressure —19·7 + 0·13 = ... 19·83 ,,
The counterpoise-bulb contained 0·0270 mgrm., or 27,000 μ mgrms. of air. Its buoyancy was altered by (19·83/760) × 27,000 = ... 703·8 μ mgrms.

But air entered the tube when it was broken; the volume of the density-tube, ascertained by previous calibration, was 0·522 cub. mm.

Weight of this air at 34·7 mm. and 17° C. = 0·522 × 1290 × 35/760 × 273/290 = ... 29·2 μ mgrms.
The sum of these quantities, 703·8 and 29·2 .. .. 733 ,,

But the pressure was changed by 19·8 mm.; this alters the weight of the density-bulb by the weight of air corresponding to the difference in volume between the glass density-bulb and a silica one; as already described, this quantity was determined directly by replacing the air-bulb by a solid counterpoise of silica, and using the density-bulb as a measure of buoyancy. For 19·8 mm. the "glass displacement" is equivalent to −32·8 μ mgrms. A further correction has to be made, viz., the change of buoyancy due to the volume occupied by the gas itself. The volume of the density-tube was 0·522 cub. mm.; the change of pressure was 19·8 mm.; hence the weight of this air for 19·8 mm. change = 0·522 × 1290 × 19·8/760 × 273/290 = 16 μ mgrms. This is a positive correction; the weight, 733 μ mgrms., must be diminished by the difference between 32·8 and 16, say, 17 μ mgrms. The remainder is 716 μ mgrms.

The last correction to make is the subtraction of the weight of the helium produced by the decay of the emanation during its stay in the weighing-tube. Now—

22,400 cub. mm. niton weigh, say, 222·5 mgrms, and
0·0224 ,, ,, weighs ,, 222·5 μ mgrms.

Each atom of niton gives three atoms of helium; hence, helium from 0·0224 cub. mm. niton weighs 12 μ mgrms. The volume of emanation decayed in the weighing-tube is 0·0887 cub. mm. - 0·0735 cub. mm. = 0·0152 cub. mm., and the weight of three times that volume of helium is 8 μ mgrms. One quarter of this has entered the glass and has not escaped, hence the helium removed weighed 6 μ mgrms. That number deducted from 716 leaves 710 μ mgrms. as the weight of the niton.

To return for a moment to its volume. The amount of niton in the weighing-tube was 0·07347 cub. mm. at the moment of pumping out. But some niton had penetrated its walls, and was not removed by the pump. That amount was estimated by comparing the γ-radio-activity of the weighing-tube after it had been weighed "empty" with that of the gas pumped off, which had, of course, diminished in radio-activity; this diminution corresponded with the time which elapsed since the last reading, and was measured to verify the constancy of the electroscope. The radio-activity of the residue left in the weighing-tube was, after correction for natural leak, 17 divisions per hour. The original radio-activity of the niton in the weighing-tube was 3996 353 = 3643 divisions per hour; its volume in the weighing-tube when decay commenced was 0·0887 cub. mm.; hence the "volume" left in the tube by the retention of niton in the walls was (17 × 0·0887)/3643 = 0·0005 cub. mm. This, subtracted from 0·07347 cub. mm., the volume of niton in the tube at the moment of pumping out, leaves 0·0730 cub. mm. as the volume actually weighed.

All the data are now complete; 0·0730 cub. mm. of niton at 0° and 760 mm. pressure weighed 710 μ mgrms. A litre weighs 9·727 grms.; a litre of oxygen weighs 1·429 grms.; and the molecular weight of niton is therefore 218.

fracture, however, was easily calculated from its known rate of decay.

As the quick-change products A, B, and C are short-lived and change rapidly into D, and as D is a solid, it remains in the density-bulb, and is not weighed, but the helium resulting from the change of niton into A, A into B, and C into D, escapes for the most part along with the niton; its weight must be calculated, and that of the escaping gas diminished by its amount, in order to arrive at the true weight of the niton.

Five experiments were made in order to determine the total loss of weight on opening the density-tube, and a sixth to obtain an estimate of the weight of the helium produced by the disintegration of the niton as far as radium D. For this purpose a density-tube was filled as described in the middle of the month of July, 1910;

it remained counterpoised on the balance until October, when the conversion into D was practically complete. As the half-life period of D is about fourteen years, it is unnecessary to consider any further change. At the end of October the point of the density-tube was broken as usual, and the tube was again weighed, the loss in weight being due to the helium produced.

We must here chronicle the fact that during the three months in which the tube hung on the balance a continuous gain in weight was noticed, rapid at first, but attaining an end-point; this amounted to 670 μ mgrms. On heating the tube, 1280 μ mgrms. were lost. The tube had not been heated before it was originally suspended on the balance; the gain was probably due to condensation of air on the electrified surface, and possibly, but improbably, to the deposition of dust. This gain of weight on standing is, however, not confined to electrified surfaces; a gold capsule, heated to redness before suspension, gained considerably in weight for two days. The density-tube was heated, and re-suspended on the balance, and for three hours there was no alteration of weight. It was then broken and immediately placed on the balance, and weighed within five minutes, during which it might be expected that no change would occur; the loss of weight was 15 μ mgrms. The volume of the density-tube was 0·196 cub. mm.; the weight of air filling it at 37·7 mm. pressure and 18·5° C. was 12 μ mgrms.; hence the total weight of helium was 27 μ mgrms.; no correction for glass displacement of air was necessary, for the pressure did not vary during the readings.

The calculated weight of helium obtainable from 0·072 cub. mm. of niton, the amount present in the tube, on the assumption that each atom (or molecule) of niton loses three α-particles on disintegrating to RaD, should have been 38 μ mgrms.; of this, only about three-quarters had been removed by the pump. It was necessary to seek for the remainder, which, we believed, had entered the glass of the weighing-tube.

Before removing it, however, we thought it worth while to attempt to dissolve the deposit of radium D from the walls of the weighing-tube, and to estimate its amount by loss. The closed end of the weighing tube was cut off, and the rest of the tube placed in the bucket along with it, and weighed. The tube itself was then washed out with a mixture of two drops of nitric acid, previously purified by distillation from a silica bulb, and one of water; the solution was preserved. The tube was then washed with water and dried by aspirating through it a current of dry air; it was then replaced in the bucket, and re-weighed. The loss was 831 μ mgrms. Supposing that the emanation, the calculated weight of which, assuming it to have the atomic weight 222·4, was 713 μ mgrms., had lost three α-particles, the weight should have been 674 μ mgrms. The difference, as we have proved by a subsequent experiment on the solubility of glass in dilute nitric acid, is due to the removal of sodium and calcium as nitrates. This must have amounted in the case given to $831 - 674 = 157$ μ mgrms. We identified under the microscope crystals of sodium nitrate.

It is obvious that no importance can be attached to the latter half of this experiment, except inasmuch as it shows a loss of weight of the order required.

The weighing-tube still contained presumably occluded helium. It was placed in a silica tube, surrounded by a thicker-walled tube, also of silica, and it was connected with a Töpler pump, and with an inverted syphon for introducing oxygen. The apparatus was freed from air, and washed out several times with oxygen, so as to avoid introducing helium or neon from the air. About one-third of a cc. of oxygen was then admitted, and the silica tube was heated in a blowpipe flame until the glass weighing-tube had completely fused; small bubbles were evolved. The oxygen, together with the gas evolved from the tube, was pumped off, and introduced into an apparatus consisting of a calibrated capillary tube in communication with a minute bulb containing charçoal cooled with liquid air. After some hours the oxygen was completely absorbed by the charcoal, and the residual gas was measured. The correction for the unmeasured gas still remaining in the charcoal bulb was found to 4 per cent. The volume was 0·042 cub. mm. at 0° and 760 mm. pressure, and its weight was therefore 8 μ mgrms. The sum of the helium actually weighed (27 μ mgrms.) plus that measured (8 μ mgrms.) gives a total of 35 μ mgrms., differing from the calculated amount (38 μ mgrms.) by only 3 mgrms. That the gas measured was pure helium was proved by surrounding the upper part of the capillary tube with tin-foil, and passing a discharge from a coil through it. The full spectrum of pure helium was seen, and no other lines.

The result has astonished us, as, perhaps, it may astonish our readers, but the conditions under which the last weighing was made were particularly favourable, since the tube was practically non-radio-active.

This experiment taught us that about one-quarter of the helium produced by the disintegration of the emanation and its products enters the walls of the weighing-tube, and is not removed by the pump; we have now all the data for calculating the density of niton. The results are given in the accompanying table.

The nomenclature of Rutherford and Soddy, which has attained the provisional assent of the Brussels Congress, is advantageous as showing the relationship between the degradation products of the various radio-active elements, but obscures any chemical relationship between the elements themselves. Were it consistently carried out, radium, which undoubtedly belongs to the group of alkaline-earth metals, would have to be named after uranium, a metal with no affinities with that group. The "emanation of radium" is a cumbrous name, and gives no indication of its position in the Periodic Table, a position which may now be taken as certain. To show its relation to gases of the argon series, it should receive a similar name; and the spectrum, the freezing-point, the boiling-point, the critical-point, the density of the liquid, and the density of the gas, the last establishing, without doubt, the atomic weight of the element, having been determined in this laboratory, it only remains to give it a name. The name "niton," Nt, which has been used in this paper, is suggested as sufficiently distinctive.

The research, of which the foregoing is an account, yields a further proof, if such were necessary, of the beautiful theory of the disintegration of the radio-active elements originally advanced by Rutherford and Soddy in 1902. The determination of the density of a gas, even with approximate exactness, has always been regarded as establishing its molecular weight, the accurate value of which may have been derived from other considerations. In the present case, these considerations are the result of the disintegration theory. Determinations by Madame Curie and by Thorpe of the atomic weight of radium show beyond all doubt that it differs little from 222·4. That four atoms of helium separate from one atom of radium is rendered almost certain from the work of Dewar, and from experiments by Rutherford, and by Ramsay and Soddy. That three atoms of helium are lost by niton on decay has been shown in the preceding pages. It follows that one helium atom must escape when radium changes into its emanation; hence the true atomic weight of the emanation must be 222·4. This number hardly differs from the mean of the atomic weight determinations given in this paper; and the disintegration theory receives a further confirmation.

Products obtained by Dissolving Phosphorus Pentoxide in Water.—D. Balareff.—When phosphorus pentoxide is dissolved in water only metaphosphoric acid is formed, and no $H_4P_2O_7$ or H_3PO_4 could be detected by analytical methods.—*Zeit. Anorganische Chemie*, lxix., No. 2.

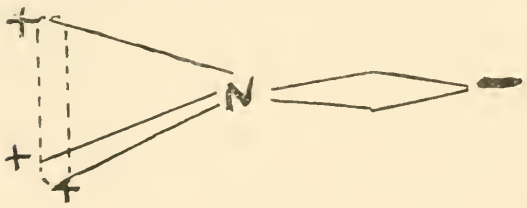
A THEORY REGARDING THE CONFIGURATION OF CERTAIN UNSATURATED BODIES AND ITS APPLICATION TO THE COBALT AMMINES AND THE CINNAMIC ACIDS.

By SARAH M. BAKER, B.Sc.

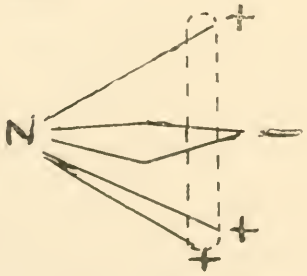
A SHORT account of this theory has already been published (Stewart, "Recent Advances in Physical and Inorganic Chemistry, 1909, p. 110) by the kindness of Dr. Stewart, whose generous interest and encouragement I should like to take this opportunity of acknowledging.

Van 't Hoff, in his famous treatise "La Chimie dans l'Espace," points out that, by applying the principles obtained on the assumption of a symmetrical space grouping of atoms, only the minimum number of possible space isomers can be obtained. The normal symmetrical grouping of atoms is probably largely brought about by some kind of electrical repulsion between the bonds or electrons which unite them. In the case of an "unsaturated" compound, two of these bonds are pulled away from their symmetrical position, and hence will exercise less repulsion on the other bonds in the molecule, and therefore the position of the latter will be altered. In a doubly bound pentavalent nitrogen atom the most likely position to be taken up by the other three groups or atoms, united to the nitrogen, is a symmetrical arrangement on a plane other than that of the nitrogen atom; when a "*d*" and "*l*" form, as found by Meisenheimer (*Ber.*, xli., 39, 66), in the case of $CH_3.C_2H_5.C_6H_5.N=O$ becomes possible.

But if the nitrogen atom is attached to three electropositive groups, and doubly bound to a strongly electronegative group, the attraction between the groups may be so great as to overcome the repulsion between the bonds, already diminished from their normal value, by their changed relative positions. Between the two extreme stable phases there would be a region of instability, and there are therefore two possible isomeric forms —



"Ex" form.



"En" form.

which we will represent as "ex" or "en," according to whether the double bond is outside the ring of atoms or surrounded by it. For convenience the isomers may be written as "ex" $H_3N=Cl—$ and "en" $NH_3=Cl—$. A violent intramolecular vibration would be the condition for the conversion of one isomer into the other.

A crude mechanical analogy will serve as an illustration. An umbrella has two stable positions, each produced by the opposition of attraction towards, and repulsion from, the handle (which figures the double bond); the spread or "en" position and the inside out, or "ex" position, with a region of instability between them.

The Application of these Principles.

1. *The Metallic Ammines.*—The two chief difficulties in representing these bodies, according to ordinary ideas of valency—the explanation of their ionisation and isomerism—are met by a slight modification of the Blomstrand-Jörgensen method of representing them, and an application of the principles of "ex" "en" isomerism. According to this system, the non-ionised acid group is attached directly to the cobalt atom, but prevented from ionising, by having also an ammino-group attached to it, after the manner of water of crystallisation, by means of the residual affinities of the atoms or groups in the acid. The ionisable acid groups are attached to one or more ammino-groups, arranged in chain formation. A series such as—

$Co\begin{cases}NH_3.NH_3X\\NH_3.NH_3X\\NH_3.NH_3X\end{cases}$ Four ions.

$Co\begin{cases}NH_3.NH_3X\\X=NH_3\\X=NH_3\end{cases}$ Two ions; possibility of isomers

$Co\begin{cases}NH_3.NH_3X\\NH_3.NH_3X\\X=NH_3\end{cases}$ Three ions; possibility of isomers.

$Co\begin{cases}X=NH_3\\X=NH_3\\X=NH_3\end{cases}$ No ions possibility of isomers.

illustrates the point.

The formulæ are confirmed by the special stability of the ammines containing unsaturated acid groups, such as $—NO_2$ and $=SO_3$ in the molecule; also by the fact that non-ionised chlorine cannot form salts with platinic chloride, which the ionisable chlorine atoms do, by means of their residual affinities.

The Isomerism among the Cobalt Ammines.—There is, according to the "ex" "en" isomerism theory, a theoretical possibility of isomerism in every cobalt ammine compound, which contains a non-ionisable acid group; because of the attraction between the acid and the hydrogen, or other atoms attached to the doubly b und nitrogen atom. Unfortunately, we know too little about the atomic forces to predict with certainty how many of these isomers would exist. It seems probable that an "ex" and "en" group, in the same molecule at the same time, would be unstable; so that one would only expect two isomers in each case. It also seems likely that there would be more probability of the two stable phases when heavier groups, such as $—CH_2—CH_2—$ or the pyridine ring, replace the hydrogen of NH_3, and when the acid part of the molecule contains more than one attracting atom as $—NO_2$ or $=SO_3$.

The Isomers which have been Observed.—Among the pentammines only one case is known; the two isomeric forms of $[Co(NH_3)_5NO_2](NO_2)_2$ (Jörgensen, *Zeit. Anorg. Chem.*, v., 169, 172). These are important, because they are inexplicable on either Werner's or Friend's theories. The only other explanation, put forward by Jörgensen, that the isomerism is due to the nitrite and nitro form of the acid group, should be taken with caution, because no metal is known to form salts of more than one form of nitrous acid.

The tetrammines have been isolated in such numbers in two isomeric forms that it is unnecessary to detail them.

Of the triammines, $Rh(NH_3)_3Cl_3$ is said to have been found in two forms, and recently Ley and Winkler (*Ber.*, 1910, xlii., 3895—3902) have isolated two isomers of the interesting internal complex salts of cobaltiglycocol, $Co(CO_2CH_2NH_2)_3$.

The platinum and chromium ammines can be represented in a similar way.

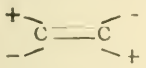
Configuration Determination among the Cobalt Ammines.—The differences in properties between the isomers are, as one would expect, chiefly in colour, solubility, and other physical properties. In chemical reactions the "en" form has the double bond more protected, so that it would be less easily opened than the more symmetrical "ex" form,

The croceo and flavo nitrito cobalt ammines behave differently when treated with concentrated hydrochloric acid. The croceo (1·6 in Werner's nomenclature) salts merely have one $—NO_2$ group replaced by —Cl, but the flavo (1·2 according to Werner) salts, besides this, have one non-ionisable acid group made ionisable by the introduction of an H_2O group into the molecule. That is, in the flavo salts, a double bond, between nitrogen and acid, has been opened. From this reaction it seems probable that the flavo salts are "ex," which is further confirmed by the fact that the only salts known of the weak carbonic acid (in which the attraction would probably not be sufficient to form an "en" isomer) are flavo or "ex" compounds.

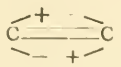
The very easy conversion of the dichlor-diethylene diammines from one to the other by acidifying or neutralising the solution, strongly confirms this dynamic method of representing them. One would expect such a change in the electrical state of the solution to be the type of force required to change the centre of vibration of the molecule; *i.e.*, to change an "ex" into an "en" isomer.

2. *The Application to certain Unexplained Cases of Isomerism among Carbon Compounds.*—From the nature of this isomerism, it is obvious that its occurrence among carbon compounds would be very rare. In the case of a malenoid and fumaroid acid, it is evident that, if one form showed "ex" "en" isomerism the other would not, because the forces acting in the two cases are very different.

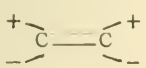
If we consider the cases of the hypothetical "en" and "ex" forms of both malenoid and fumaroid isomers of an acid, we get the four forms:—



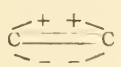
"Ex" fumaroid.



"En" fumaroid.



"Ex" malenoid.

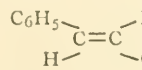


"En" malenoid.

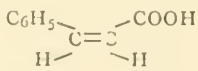
The conditions necessary for the existence of two isomers, in any case, are that there should be two regions of comparatively stable equilibrium with a region of instability between them. These conditions are not fulfilled in the fumaroid isomer (which, at first sight, seems the more likely to show "ex" "en" isomerism because of the proximity of the attracting groups), because the horizontal attraction between the positive and negative groups increases regularly as they approach, and there is no special increase after passing the vertical to counterbalance the large vertical repulsion between the bonds. In the malenoid isomer, on the other hand, the attracting forces between the groups being nearly vertical, decrease as the vertical position is approached, and increase again rapidly after passing the vertical as the "en" position is approached. If there is not too much repulsion between the positive and negative groups approaching on the same side of the molecule, there is a possibility of two isomers of this kind in the malenoid form, but it would be exceedingly rare. In the case of cinnamic acid, the only hitherto observed example of this kind, the two large electronegative groups, —COOH and $—C_6H_5$, cannot be considered as having a very great mutual repulsion; they may even attract one another.

The Observed Facts in the Case of the Cinnamic Acids (Michal, *Ber.*, xxxiv., 3656).—Instead of two isomers, as would be expected on the usual hypothesis, there are three well defined isomeric forms of cinnamic acid. Ordinary cinnamic acid is the fumaroid form from its physical properties, but in chemical properties it is less stable than allocinnamic acid. This latter is apparently one isomer of the malenoid form, while isocinnamic acid is the less stable malenoid isomer.

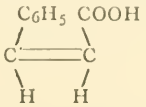
Granting the possibility of "ex" "en" isomerism, these facts not only present no anomalies, but are exactly what one would expect. Isocinnamic acid is the ordinary "ex" malenoid cinnamic acid, and as such is less stable than its "ex" fumaroid isomer. But being capable of existing in the "en" form, allocinnamic acid, isocinnamic acid is converted into this more stable isomer on standing. The "en" malenoid allocinnamic acid, having its double bond more protected than the "ex" fumaroid isomer, will be less easily attacked by bromine. This is in accordance with the facts. Also it will be much harder to convert into the "ex" fumaroid isomer than is the case with most malenoid compounds. This also is the case, for "allocinnamic acid can be repeatedly melted without any considerable amount being converted into ordinary cinnamic acid." The three formulæ—



Ordinary cinnamic "ex" fumaroid.



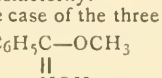
*iso*Cinnamic "ex" malenoid.



*allo*Cinnamic "en" malenoid.

therefore represent the physical and chemical properties of these three isomers satisfactorily.

It is possible that the case of the three isomers of—



(Lossen, *Ann.*, 1894, 281, 199; and 1894, 282, 226; Werner, *Ibid.*, 1896, 29, 1150; and Subak, *Ibid.*, 1896, 1153) may be due to the same type of isomerism, the groups attached to the carbon atom being attracted into the "en" position by the nitrogen atom.

As it has been shown that, without departing from the ordinary ideas of valency and chemical affinity, a simple explanation can be given, not only of the behaviour and isomerism of the metallic ammines, but also of certain hitherto unexplained cases of isomerism among carbon compounds, it seems unnecessary to invent a new system of valency and chemical behaviour to explain what has been observed among the metallic ammines.

It is highly improbable that this precise mode of representing so intricate a matter as the balance of forces in a molecule is correct, but if it shows the facts in a new light or opens the way to the true solution of the problem it will not have been put forward in vain.

I have much pleasure in thanking Miss K. A. Burke for her kind advice and encouragement.

NOTE ON A RECENT METHOD FOR SEPARATING TANTALUM AND COLUMBIUM.

By H. W. FOOTE and R. W. LANGLEY.

A new method of separating tantalum from columbium was proposed recently by Weiss and Landecker (*Zeit. Anorg. Chem.*, 1909, lxiv., 65). This method consists essentially in fusing the mixed oxides with sodium carbonate containing a little nitrate, and treating with hot water. Some tantalum, as sodium tantalate, remains insoluble, and is removed by filtering and treated separately. The tantalum remaining in solution is precipitated by carbon dioxide. The authors state that if the conditions are properly adjusted, all the tantalum is precipitated, leaving columbium in solution. On the other hand, Rose ("Handbuch Analyt. Chem.," 6th ed., ii., 339) and Ostwald ("Grundlinien Anorg. Chem.," ed. 1900, 726) state that both are completely precipitated by carbon dioxide from a sodium carbonate solution.

We have tried a considerable number of experiments following the directions given by Weiss and Landecker as

No.	Ta_2O_5 taken.	Cb_2O_5 taken.	Ta_2O_5 found.	Cb_2O_5 found.	Na_2CO_3 used for fusion.	$NaNO_3$ used for fusion.	Volume when CO_2 was passed in.	Remarks.
	Grm.	Grm.	Grm.	Grm.	Grms.	Grm.	Cc.	
1.	0·2100	0·0900	0·3025	None	2·00 (about)	0·1 (about)	600	
2.	0·2129	0·0913	0·3219	0·0117	0·58	0·05	250	
3.	0·1975	0·0846	0·2903	0·0125	1·2	0·05	250	A precipitate separated on standing over night before passing CO_2.
4.	0·2465	0·0616	0·3167	0·0030	0·6	0·05	250	Precipitate with CO_2 separated in one hour; stopped CO_2 in one and a-half hours.
5.	0·2362	0·0591	0·2974	0·0056	1·2	0·05	250	
6.	0·2580	0·0645	0·3193	0·0167	1·8	0·05	250	
7.	0·2546	0·0637	0·3220	0·0087	1·8	0·05	250	Fused mass when treated with water contained many crystalline plates.
8.	0·2728	0·0682	0·3425	0·0037	1·8	0·1	250	
9.	0·2838	0·0710	0·3654	Trace	1·8	0·1	250	Precipitate with carbon dioxide became crystalline on boiling.

closely as possible, but varying certain conditions not defined by the authors. We were unable to make any satisfactory separation by this method. On the contrary, in every case nearly all the columbium precipitated with the tantalum. The authors state that a separation depends upon adjusting the amounts of reagents used, the method of fusion, and the concentration of the solution within narrow limits. These conditions, in our experiments, were adjusted to conform as closely as possible with the slightly indefinite directions given by the authors. The quantities of reagents and the concentration of solutions were also varied somewhat to effect a separation if possible. The method—taken from Weiss and Landecker—was as follows:—The amounts of reagents used will be given in the table. About 0·3 grm. of a known mixture of tantalic and columbic oxides was fused with sodium carbonate over a blast till effervescence ceased. Sodium nitrate was added, and the fusion continued about ten seconds. The fusion was treated with hot water on the steam-bath for two hours, and the insoluble residue filtered and washed with 5 per cent sodium bicarbonate solution. The filtrate, containing columbium and tantalum, was cooled, and carbon dioxide passed in until no further precipitate formed. In the meantime, the insoluble sodium tantalate was boiled with dilute sulphuric acid and hydrogen dioxide to dissolve it. We were never successful in getting complete solution at this point. Sulphurous acid was added, and the solution kept warm for two hours to re-precipitate the dissolved tantalum. The precipitate was filtered, washed, ignited, and weighed. The oxide precipitated with carbon dioxide, which should have been pure tantalic oxide, was filtered, and the weight after ignition added to the weight of tantalic oxide already obtained.

The filtrate from the carbon dioxide precipitation was acidified with sulphuric acid, an excess of sulphurous acid added, the solution boiled, and allowed to stand. The precipitate which should have contained all the columbium was filtered, washed, ignited, and weighed. As a precaution ammonia was added to the filtrate to be sure that no columbium was left in solution.

The results of these experiments are tabulated. They show that we obtained no separation in any case, but that columbium was almost quantitatively precipitated with the tantalum by carbon dioxide. The precipitate must have carried some alkali with it, as the amount of tantalum and columbium oxides recovered was always apparently greater than the amount used. The results of the experiments are given in the accompanying table.

The results have convinced us that the method in its present form is unreliable, but it is possible that other conditions can be found which will permit a separation. If this could be done the method would be exceedingly valuable.—*American Journal of Science*, xxx., No. 180.

THE CHANGE OF COBALTOUS INTO COBALTIC NITRITE.

By TSUNEO SUZUKI.

VERY little is known of what happens to cobaltous nitrite when it is produced in solution in the absence of acids or dissolved salts. In 1860 the Swedish chemist, Lang, published the fact that such a solution of cobaltous nitrite left on evaporation blackish brown crystals of highly basic cobaltic nitrite (*K. S. Vet. Akad. Handl.*, 1860; *Pogg. Ann.*, 1863, cxviii., 282). According to Hampe (*Annalen*, 1863, cxxv., 343), the red saline mass thus obtained contains cobaltous as well as cobaltic nitrite. Neither Lang nor Hampe gave quantitative results.

In order to get Lang's crystals, precipitated calcium carbonate suspended in a very little water was dissolved up by passing in nitrous gases, cobalt sulphate in equivalent quantity was added, and the calcium sulphate filtered off. Lang and Hampe both used barium nitrite, but the difficulty of separating barium sulphate, when precipitated from a cold neutral solution, made the use of calcium nitrite be preferred in the present research. The filtrate from the calcium sulphate was evaporated almost to dryness in a vacuum desiccator at a temperature of 30°, and the residue treated with a little water, filtered from some calcium sulphate, and left in the desiccator to again crystallise. The salt is too changeable to be safely re-crystallised. It forms small very dark red crystals, very soluble in water, and remarkable for being alkaline to litmus.

To analyse the salt the cobalt was precipitated as cobaltous ammonium phosphate and weighed as cobaltous pyrophosphate (Dirvell and Clarke's process as given in Dittmar's *Quantitative Analysis*, p. 309). The little cobalt left in solution was obtained by adding a drop of ammonium sulphide, and burning the cobalt sulphide to the black oxide, CO_3O_4. The cobaltic cobalt in the salt was separately determined by digesting the salt with a concentrated warm solution of sodium carbonate and treating the residue twice with fresh sodium carbonate, the last time bringing the whole to boiling. The washed residue was dissolved in dilute hydrochloric acid holding potassium iodide in solution and the cobalticum estimated iodometrically. The nitrite of the salt, which had been converted by the sodium carbonate into sodium nitrite, was estimated by the permanganate method.

The results of analysis are expressed by the formula: $Co''_{14}Co'''_6(NO_2)_{30}(OH)_{16},34H_2O$, in which Co:N = 2:3 and the ratio of the valencies of the cobalt to those of the nitrogen atoms are as slightly more than 3:2. The percentage numbers are given in the following table;—

	Found.	Calculated.
Total cobalt	34·13	34·26
Cobaltic cobalt ..	10·42	10·28
Nitrogen	12·31	12·21

The formula calculated for the salt is resolvable into—

$$2Co''_4Co'''_2(NO_2)_{10}(OH)_4 + Co''_6Co'''_2(NO_2)_{10}(OH)_8 + 34H_2O,$$

and in other similar ways from what is known of cobaltic and other allied compounds, these constituent salts may have their formulæ expanded into the following, as probably accurate expressions of their constitution :—

$$Co''_4Co'''_2(NO_2)_{10}(OH)_4 = (NO_2Co''NO_2NO_2)_3{\equiv}Co'''\begin{matrix}OH\\(OHOHCo''NO_2),\\OH\end{matrix}$$

$$Co''_6Co'''_2(NO_2)_{10}(OH)_8 = (NO_2Co''NO_2NO_2)_3{\equiv}Co'''_2\begin{matrix}(OHOHCo''OH)\\(OHOHCo''NO_2).\\(OHOHCo''OH)\end{matrix}$$

It is unnecessary to add to these formulæ the complex one for the crystalline salt as compounded of them. The apposition in them of NO_2 with NO_2 and of OH with OH serves to express, without pretending to explain, the pairing of acidic components so characteristic of such double salts as nitrites and cyanides. The NO_2 and OH groups next on either side to the CO'''_2 group represent, together with it, hemihydroxycobaltic nitrite, $(NO_2)_3Co'''_2(OH)_3$, existent probably only in combination as a double nitrite. Cobaltous nitrite and hydroxynitrite are similarly displayed in these formulæ.

The self-conversion of cobaltous nitrite into cobaltic nitrite, merely, would be shown by the equation : $Co''(NO_2)_2H_2O = Co'''(NO_2(OH)_2 + NO$, did all the cobalt nitrite ever become cobaltic, instead of but little more than one-third of it. As, however, the whole of the cobalt nitrite undoubtedly takes part in the change, this fact must be presented in the equation framed to express the conversion. This equation will be more readily followed by prefacing it with another, showing part of the change :

$$3Co''(NO_2)_2 + 2H_2O = Co''(NO_2)_3(OH)_3, Co''(NO_2)(OH) + 2NO,$$

from which it will be seen that two cobalt atoms, in becoming cobaltic, pair together and lose only one nitroxyl group, the third cobalt atom remaining cobaltous though also losing a nitroxyl group. The equation of the actual change is $6Co''(NO_2)_2 + 2H_2O = Co''_4Co'''_2(NO_2)_{10}(OH)_4 + 2NO$, in which—

$$Co''_4Co'''_2(NO_2)_{10}(OH)_4 = 3Co''(NO_2)_2, Co'''_2(NO_2)_3(OH)_3, Co''(NO_2)(OH).$$

That is, 6 molecules of cobalt nitrite become united, half of them unaltered and the other three, with loss of 2NO and acquisition of $2H_2O$, as cobaltic and cobaltous hemihydroxy-nitrites. This condensation of the 6 molecules into a complex happens without any union taking place of the atoms of cobalt with each other through the agency of their ordinary valencies, which are, it will be seen, used up in the union of the cobalt with nitroxyl and hydroxyl atoms.

The change just formulated must be treated as indivisible, but other changes occur which may be regarded as secondary to it. There is evidently a cumulative resolution of the molecules of the $Co''_4Co'''_2(NO_2)_{10}(OH)_4$ into others simpler by having given up some or all of their cobaltous hydroxynitrite, and others enriched by having received this additional cobaltous hydroxynitrite. This resolution is attended with another one, that of some of the cobaltous hydroxynitrite into nitrite and hydroxide, the latter retained by the hydroxycobaltinitrite, the former lost to it by undergoing conversion itself to cobaltinitrite in a way similar to the original change. These subsidiary changes may be attributed in part to the force of crystallisation, but are principally to be referred to the feeble hold of the cobaltinitrite upon much cobaltous hydroxynitrite against the tendency of this to become itself cobaltic. The last stage, therefore, of the conversion of cobaltous nitrite into the crystals obtained is to be expressed by—

$$7Co''_4Co'''_2(NO_2)_{10}(OH)_4 = 2Co(NO_2)_2 + 4Co''_3Co'''_2(NO_2)_9(OH)_3 + Co''_{14}Co'''_6(NO_2)_{30}(OH)_{16},$$

the crystalline substance, $Co''_{14}Co'''_6(NO_2)_{30}(OH)_{16}$, being itself a compound of $3Co''_3Co'''_2(NO_2)_9(OH)_3$ with $3Co(NO_2)(OH)$ and $2Co(OH)_2$.

In accordance with the remarkable constitution of the crystalline salt, indicating as it does that atoms of hydroxyl-like nitroxyl groups can pair together between cobaltic and cobaltous atoms, is the behaviour of the salt when it is acted upon by half the quantity of an alkali carbonate equivalent to its cobaltous atoms. Out of 23·7 parts per cent of cobaltous cobalt present in the salt, 14·1 parts were precipitated in this way. The equation expressing this result is—

$$Co''_{14}Co'''_6(NO_2)_{30}(OH)_{16} + 7K_2CO_3 = 8KNO_2 + 7CoCO_3 + 1{\cdot}5Co(OH)_2 + 2K_3Co'''_2(NO_2)_6(OH)_3 + Co''_3Co'''_2(NO_2)_9(OH)_3{<}\begin{matrix}OHCo''NO_2\\(OHCo''OH)_{1\cdot5}.\end{matrix}$$

For 1·5 theory requires 2, and, since partial precipitation in this way can hardly lay claim to great accuracy, the cobaltous hydroxycobaltinitrite may allowedly be written as (see above)—

$$Co''_6Co'''_2(NO_2)_{10}(OH)_8.$$

A potassium cobaltous salt is obtained by adding a solution of potassium carbonate, just so long as it continues to cause immediate precipitation, to the solution of cobaltous nitrite after its spontaneous conversion into hydroxycobaltinitrite, filtering, and gradually mixing the red-coloured filtrate with about twice its volume of absolute alcohol. The potassium cobaltous salt is thus obtained as a rose-coloured flocculent precipitate, which is very soluble in water and not stable in the air or in solution. Washed with alcohol and dried in a desiccator it was found to have the composition expressed by $K_6(NO_2)_6Co''Co'''_2(OH)_8,5H_2O$. The calculated numbers are for this formula, after deducting $K_{0\cdot3}$ and adding in its place $H_{0\cdot3}$, the salt as prepared showing a deficiency of one-twentieth of the six atoms of potassium :—

	Found.	Calculated.
Total cobalt	19·56	19·62
Cobaltic cobalt ..	12·82	13·08
Potassium	24·73	24·72
Nitrogen	9·36	9·32

Only in the case of the cobaltic cobalt, and then but slightly, do the calculated numbers differ appreciably from the numbers found.

The empirical formula is remarkable in that it can be broken up into $6KNO_2 + Co_3(OH)_8 + 5H_2O$. The constitutional formula of the salt is that of a hexa-potassium hydroxycobaltous hydroxycobaltinitrite :—

$$(KNO_2NO_2)_3{\equiv}Co'''_2\begin{matrix}OHOHK\\OHOHCo''OHOHK,5H_2O.\\OHOHK\end{matrix}$$

The equation satisfactorily expressing the interaction, so far as it is yet worked out, between a solution of transformed cobalt nitrite and potassium carbonate is the following :—

$$5Co''_4Co'''_2(NO_2)_{10}(OH)_4 + 19K_2CO_3 = 19CoCO_3 + 20KNO_2 + 4K_3Co'''_2(NO_2)_6(OH)_3 + K_6Co''Co'''_2(NO_2)_6(OH)_8.$$

But this equation assumes the existence of the simple potassium hydroxycobaltinitrite $(KNO_2NO_2)_3Co'''_2(OH)_3$, which may be doubted.

With a dilute solution of silver nitrate the solution of transformed cobalt nitrite yields a straw-yellow precipitate, which is slightly soluble in water, giving it an orange-

yellow colour. It is unstable when moist, changing into silver nitrite and basic cobaltic products. Its composition agrees well with the formula, $Ag_3Co'''_2(NO_2)_6(OH)_3$:—

	Found.		Calculated.
Silver	42·12	41·97	42·13
Cobalt	15·61	15·56	15·35
Nitrogen	10·70	10·66	10·92

The analyses were made on different preparations of the salt. Sometimes, instead of the salt or with it, silver nitrite and cobaltic precipitates are formed. The simplest equation for expressing the interaction in which the silver hydroxy cobaltinitrite is alone precipitated is—

$$2Co''_4Co'''_2(NO_2)_{10}(OH)_4 + 6AgNO_3 = Co(OH)_2 + \\ + 4Co(NO_2)_2 + 3Co(NO_3)_2 + 2Ag_3Co'''_2(NO_2)_6(OH)_3,$$

it being understood that the cobaltous hydroxide remains in solution in combination with undecomposed hydroxycobaltinitrite, and that the cobaltous nitrite similarly combines or else proceeds to pass of itself into hydroxycobaltinitrite. The constitutional formula of the silver salt is $(AgNO_2NO_2)_3Co'''_2(OH)_3$.

The three salts which have been obtained in this investigation of the change undergone by cobaltous nitrite in aqueous solution, namely, hydroxycobaltous hydroxycobaltinitrite, potassium hydroxycobaltous hydroxycobaltinitrite, and silver hydroxycobaltinitrite, are not the first of the hydroxycobaltinitrites which have been prepared and examined. But the method of getting these others differed from that used in the present work, in that the first step was the dissolution of cobalt carbonate in presence of water by the action of the nitrous gases from nitric acid and arsenious oxide. By taking the nitrite or carbonate of another metal with the cobalt carbonate, double salts were obtained. The salt of the other metal was taken in the proportion of three equivalents to two of cobalt carbonate, so that by passing in the nitrous gases long enough, normal cobaltinitrites could be and were thus prepared by Rosenheim and Koppel, who introduced this method of getting cobaltinitrites and hydroxynitrites, and prepared several of them for the first time (*Zeit. Anorg. Chem.*, 1898. xvii., 35). The hydroxycobaltinitrites they obtained and analysed were a cobaltous, a barium, a strontium, a zinc, and a silver hydroxycobaltinitrite, whilst others were met with.

It will be seen that the method followed in preparing these hydroxycobaltinitrites is not well suited for the investigation of the problem which is the subject of the present paper. For, in presence of nitrous acid and nitric peroxide, there will occur some neutralisation of basic nitrite by the former—

$$Co(NO_2)(OH) + HNO_2 = Co(NO_2)_2 + H_2O,$$

and possibly some production of cobaltic nitrite from cobaltous nitrite and nitric peroxide—

$$Co(NO_2)_2 + NO_2 = Co(NO_2)_3,$$

whereby the nature of the self-transformation of the cobaltous nitrite becomes obscured and the course of the change interfered with. Another objectionable feature of this mode of preparing hydroxycobaltinitrites is the production of more or less nitrate, which seems unavoidable.

In spite of the comparative unsuitability of their process from the point of view of this paper, it was necessary to repeat, if possible, some of Rosenheim and Koppel's work, the results of which were hardly consistent with those which had been got by using the Lang process. The cobaltous salt they have described was apparently indistinguishable from that now described in this paper (see above) except in composition. A re-examination of the cobaltous salt thus prepared was therefore decided upon.

Nitrous gases were passed into water holding cobalt carbonate suspended until dissolution of the latter was nearly complete. The filtered solution was evaporated under reduced pressure at 30°, and yielded the expected crystals which were analysed. The results agree well with Rosenheim and Koppel's, except that the latter did not include any finding for the cobaltic element, the proportion of it present being assumed by them to be two-fifths of the total cobalt. Calculation for—

$$Co''_4Co'''_2(NO_2)_8(NO_3)_2(OH)_4,15H_2$$

gives figures which, with those here obtained and those found by Rosenheim and Koppel, are as follows :—

	Found.	Calculated.	Rosenheim and Koppel found.
Total cobalt ..	30·27	29·90	30·15
Cobaltic cobalt ..	9·80	9·97	-
Total nitrogen ..	11·77	11·82	11·65
Nitrite nitrogen ..	9·31	9·46	8·90

Rosenheim and Koppel gave the salt a formula equivalant to $Co''_2Co'''_2(NO_2)_6(OH)_4,Co(NO_3)_2,12H_2O$; but this can be set aside, now that the ratio Co'':Co''' has been experimentally determined. In the light thrown upon the constitution of the hydroxycobaltinitrites by the work described in the present paper, the constitution of this nitrate-containing cobaltous salt may be expressed by—

$$\begin{matrix} NO_3Co''NO_2NO_2 \\ NO_2Co''NO_2NO_2 \\ NO_3Co''NO_2NO_2 \end{matrix} \diagdown \diagup \begin{matrix} OH \\ Co'''_2 \\ OH \end{matrix} OHOHCo''NO_2,15H_2O$$

which differs from the formula already given only in having $2NO_3$ in place of $2NO_2$. But the crystals obtained from the solution prepared by Lang's method were more basic than this, and, in accordance with this difference, it was found that the crystals obtained from the solution prepared by Rosenheim and Koppel's method do not, when treated with solution of sodium carbonate equivalent to half their cobaltous element, give a precipitate containing noticeably more than half the cobaltous element. In the case of the crystals from the Lang solution, the precipitate, similarly obtained, did include much more than this, though not as much as the formula indicated might have been precipitated. In that case some, in this case all, the cobaltous hydroxide remained in solution as a more basic hydroxycobaltinitrite (see above).

From the Rosenheim and Koppel solution the same potassium hydroxycobaltous salt and the same silver salt were obtained as from the Lang solution. In the statement mentioned above the second analysis of the silver salt was made on a precipitate from such a solution. Rosenheim and Koppel failed to get from it anything but silver nitrite in this way, though they got a different greyish brown microcrystalline hydrated silver hydroxycobaltinitrite, indirectly through a zinc hydroxycobaltinitrite prepared in their way. To their silver salt, and the other hydroxycobaltinitrites described by them, they have given formulæ equivalent to—

$$Ag_4Co'''_2(NO_2)_6(OH)_4 + H_2O,$$
$$Ba_2Co'''_2(NO_2)_8(OH)_2 + 0{\cdot}2Co(NO_3)_2 + 11H_2O,$$
$$Sr_2Co'''_2(NO_2)_8(OH)_2 + 10H_2O,$$
$$Zn_2Co'''_2(NO_2)_6(OH)_4 + 9H_2O.$$

But more evidence is wanted to carry conviction as to the existence of such differences as those presented between the formulæ of the strontium and zinc salts and between the composition of Rosenheim and Koppel's series of salts and that of the salts now described. There is no evidence recorded in their paper as to whether the presence of additional nitrogen as nitrate was tested for in any other case than that of the barium salt, although in all cases the mother-liquor of the salt contained nitrate. Also evidence is wanting of the proportion of cobaltic element in the salts. As a consequence of the latter omission in the paper, and by taking the more probable view that the nitrate in the barium salt was that of barium rather than of cobalt, the formula—

$$Ba_2Co''Co'''_2(NO_2)_{10{\cdot}8}(OH)_{1{\cdot}2},0{\cdot}73Ba(NO_3)_2,25{\cdot}5H_2O,$$

can be given to their second preparation of the barium salt, and with markedly closer approximation to the results of analysis than that reached by their formula. Their silver

salt, in which it is improbable that either cobaltous metal or nitrate was present, may have its given formula rearranged so as to make it appear as a derivative of the silver salt, $(AgNO_2NO_2)_3Co'''_2(OH)_3$, here described, thus—

$$(AgNO_2NO_2)_3Co'''_2(OH)_3(OH)Ag,H_2O.$$

It has not been found possible to get time and opportunity to extend this research by further work upon Rosenheim and Koppel's solution and its derivative hydroxynitrites or upon Lang's solution. But enough has been accomplished probably to justify the expectation that all hydroxycobaltinitrites will prove to be of the type of the salts met with in this investigation.

The author is greatly indebted to Prof. T. Haga for valuable advice given him during the course of this work, and to Prof. E. Divers, F.R.S., for assistance in expressing the significance of the results of the experiments, and in preparing the text of the paper.—*Journal of the College of Science, Imperial University, Tokyo, Japan*, xxviii.

NOTICES OF BOOKS.

The Encyclopædia Britannica: A Dictionary of Arts, Sciences, Literature, and General Information. Eleventh Edition. Cambridge: At the University Press. 1910.

(Engineering).

On February 3rd we gave a preliminary notice of this work, drawing attention to the general plan upon which it is based, and dealing particularly with the subject of chemistry. We now propose to deal separately with some of the more important sections so as to call attention to the magnitude and value of the work. The section of Engineering is of vast national and commercial importance, and is presented in great detail. In a brief introductory notice, "Engineering" is described as "the art of directing the great sources of power in nature for the use and convenience of men." These sources of energy are divided into three main sections:—The Energy of Wind, The Energy of Water, The Energy of Fuel. Articles upon the first two, under the heading of Hydrostatics and Windmill, are from the pen of Prof. W. C. Unwin, and present in a masterly way practically all that can be told upon the subject. The section upon hydrostatics is based on the article by the same author in the Ninth Edition, but has been enlarged so as to cover the latest developments in water turbines and hydrostatic machines. This article occupies no less than 74 pages, and contains 213 illustrations, commencing with the properties of fluids and the flow of liquids, illustrated by many examples of the line-of-flow method of Prof. H. S. Hele Shaw. The author gives complete mathematical and practical explanations of the friction of liquids, its flow in pipes and canals, current meters and methods of gauging streams, water-meters, turbines, and centrifugal pumps and motors. Fuels are treated separately in three sections, Solid, Liquid, and Gaseous. The first, under the head of Coal, is by H. Bauerman, and occupies eighteen pages, commencing with its history and physical properties, and giving interesting statistics upon the coal question. The estimated amount of coal in Great Britain is in round numbers one hundred thousand million tons, with a possibility of an extra forty thousand millions in unproved and possible coal fields. At the present rate of annual increase in consumption this may last from 200 to 250 years—and then? The article gives full illustrated details of the various methods of mining, mine working, and coal conveying. In connection with the sinking of shafts through soft ground or water-bearing rock to reach the coal seams the ingenious method introduced in 1883 by Poetsch is described. This consists in circulating brine cooled to 5° F. through a series of vertical pipes, closed at the bottom, contained in bore-holes arranged at equal distances apart around the space to be frozen. By this means a hard hollow cylinder of frozen ground is formed, inside which the ground can be broken by hand or by blasting in the same manner as hard rock. An interesting application of X-rays has been made for demonstrating the stratified or other formation of the ash in coal, the combustible portion being transparent and the ash opaque. The article concludes with a statement of the loss of life in coal-mining in the year 1906, and it is there seen that terrible as are the frequent disasters due to explosions the loss of life from that cause is only about 4 per cent of the total. The list given is as follows:—

From explosions	54
Falls of ground	547
Other underground accidents ..	328
Accidents in shafts	65
Surface accidents	135
Total	1129

As, however, no estimate is given of the number of men employed the risk of this occupation cannot be estimated.

The subject of Boilers by T. J. Milton occupies twelve pages, and gives full details of the various types of boiler now in use for stationary, locomotive, and marine purposes. Steam Engine, by Prof. J. A. Ewing, is based on a similar one in the Ninth Edition, but is enlarged in the section dealing with steam, turbines, and superheaters. Oil Fuel is the work of Sir Fortescue Flannery, and the occurrence of Liquid Fuel and methods of sinking wells are fully treated by Sir Boverton Redwood. The third section, Gaseous Fuel, contains an article on Gas by Prof. Lunge; Gas and Oil Engines are described by Dugald Clerk. The history of the famous Otto Gas Engine occupies a prominent place, but much information about other forms of internal combustion engines is given, notably the Clerk Cycle Engine. To show the advance in efficiency of the four-cycle "Otto" engine from 1882 to 1908 a table is given where it is shown that the Brake-thermal Efficiency, *i.e.*, the effective efficiency of the engine for doing work, has been increased from 14 per cent to 32·2 per cent. The efficiency of the two-cycle engine falls below this.

Following the production of mechanical power by these means, the next section treats of Power Transmission, and this is divided into mechanical, pneumatic, hydraulic, and electrical transmission. The authorities here are Prof. W.E. Dalby, A. de W. Foot, E. B. Ellington, and Dr. Louis Bell. The important section dealing with Electrical Transmission is the work of Prof. J. A. Fleming, C. G. Hawkins, and Dr. Louis Bell.

In the utilisation of fuels other than the conversion into mechanical power, there is a comprehensive article upon Warming Houses and Domestic Hot-water Supply, but the most important works under this heading are those dealing with Gas and Electric Lighting by Profs. V. B. Lewes and J. A. Fleming.

Engineering and Transport.—The main divisions of this section naturally concern Shipping, Railway, and Electric transport; each department is of supreme national importance, and is dealt with in an exhaustive manner. Shipbuilding has an antiquarian and historical sketch by Dr. Edward Warre, and then the main subject is taken up by Sir Phillip Watts, Chief Constructor to the Admiralty. There is also a short and interesting sketch under the head of Compass by Prof. Silvanus P. Thompson, who has given much attention to the puzzles of the early history of the subject. Then follows a long and important article upon Dredging, the first and main portion being occupied by description and illustration of the various engineering devices that have been evolved for dredging rivers and canals, notably the Suez and the Panama canals, and the article concludes with a most interesting *résumé* upon dredging from the marine biologist's point of view. The results of the work of various expeditions that have been equipped for ascertaining the geological distribution of marine life have shown that the early idea that the zero line of animal life was reached at about 100 fathoms was erroneous, and at the greatest depth at which it has been

possible to work, that of some 2½ miles in the Bay of Biscay, the dredge brought up well developed representatives of all the classes of marine invertebrates. One cannot help speculating as to the possible mental sensation of some fortunate Echinoderm upon being suddenly raised from its dark environment at the ocean bottom to the sorting-table of a ship's deck! The article on Dredging closes with a report of the work of H.M.S. *Challenger*. Under the heading Railways is found a long composite article, chiefly by American authors. In this article the whole of the vast subject of Tramways, Bridges, and Tunnels is presented. Aeronautics is a section well worth studying, and is the work of J. W. L. Glaisher and the late J. Bell Pettegrew. Under Aerostation the history of the discovery and evolution of the balloon is given in detail with many illustrations, from the first hot-air balloon invented by Joseph Montgolfier in 1740 down to the successful dirigibles of Count Zeppelin in recent time.

MISCELLANEOUS.

The Royal Society.—The following fifteen candidates have been selected by the Council to be recommended for election into the Royal Society:—Prof. H. T. Barnes, Prof. A. J. Brown, Prof. J. B. Cohen, Prof. W. E. Dixon, Prof. F. G. Donnan, Major E. H. Hills, Dr. W. H. Lang, Prof. J. B. Leathes, Prof. E. A. Minchin, Prof. R. Muir, Mr. R. D. Oldham, Mr. R. I. Pocock, Prof. A. W. Porter, Mr. H. W. Richmond, and Mr. G. G. Stoney.

Reactions in presence of Nickel.—Panchánan Neogi and Birendra Bhusan Adhicány.—The authors have repeated Ramsay and Young's experiment, and have found that nitrogen and hydrogen do not unite to form ammonia in presence of iron nor in presence of nickel when every precaution is taken to remove all traces of nitric oxide. Nitric oxide and sulphur dioxide can be directly reduced by hydrogen in presence of nickel, while phosphorus pentoxide undergoes an indirect reduction, phosphides being formed as intermediate products.—*Zeit. Anorg. Chem.*, lxix., No. 2.

NOTES AND QUERIES.

"*" Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

New Ferments.—Can any reader inform me where I can procure a small supply of the newly-discovered ferments, *Amylomyces Rouxii*, and the various Japanese yeasts?—E. G. BRYANT.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "The Industry of Brewing," by A. C. Chapman.
—— Royal Society of Arts, 8. "Applications of Electric Heating," by Prof. J. A. Fleming, F.R.S.
TUESDAY, 7th.—Royal Institution, 3. "Crystalline Structure—Mineral, Chemical, and Liquid," by A. E. H. Tutton.
WEDNESDAY, 8th.—Royal Society of Arts, 8. "Plague and its Dissemination," by J. Cantlie, M.A.
THURSDAY, 9th.—Royal Institution, 3. "Ruskin," by A. C. Benson.
—— Royal Society. "Absorption Spectra of Lithium and Cæsium" and "Dispersion in Vapours of the Alkali Metals," by P. V. Bevan. "The Ionic Solubility Product," by J. Kendall. "Electrical Waves occurring in Nature," by Dr. W. H. Eccles and H. M. Airey.
FRIDAY 10th.—Royal Institution, 9. "Recent Advances in Turbines," by The Hon. Charles A. Parsons, C.B., F.R.S.
—— Physical, 8. Demonstration of the Working of the Gyro Compass, by G. K. B. Elphinstone. "An Electrical Trevelyan Rocker," by Dr. W. H. Eccles. "The Tilted Gold-leaf Electroscope," by Dr. G. W. C. Kaye.
SATURDAY, 11th.—Royal Institution, 3. "Radiant Energy and Matter," by Prof. Sir J. J. Thomson, F.R.S.

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THE CHEMICAL NEWS.

Vol. CIII., No. 2676.

STUDIES OF THE PROCESSES OPERATIVE IN SOLUTIONS.

XIX.—The Complexity of the Phenomena afforded by Solutions: a Retrospect.

With an Addendum on Non-aqueous Electrolytes.

By HENRY E ARMSTRONG.

(Concluded from p. 99).

It is necessary to draw a distinction between solutions which behave as electrolytes and those which do not; some change is involved in the formation of the one that is not involved in the formation of the other. Putting salts aside, substances generally are non-conductors: what happens when they are dissolved in water? The behaviour of hydrogen chloride and alcohol may be taken as typical of the two classes into which substances are divisible—those which are and those which are not potentially electrolytes. The assumption I have advocated (Part VI.) is that in the case of the former certain molecules interact in two ways:—

$$HCl + OH_2 \rightleftharpoons HCl{<}^{H}_{OH} \qquad HCl + OH_2 \rightleftharpoons H_2O{<}^{H}_{Cl}$$

That is to say, both molecules are *distributed*—both are potential electrolytes. In the case of alcohol, only one of the molecules is distributed, if indeed *hydrolation* take place at all:

$$OHEt + OH_2 \rightleftharpoons HEtO{<}^{H}_{OH}$$

In both cases, a certain proportion of the molecules, depending on the conditions, become *hydronated*, perhaps, in a variety of ways.

My further assumption is that, generally speaking, the hydrolated molecules are the active constituents of a solution—that the *process of activation* attending dissolution in water is one involving and dependent on the formation of hydrols.

Electrolysis, in my opinion, is the outcome of the interaction of the hydrol $R'X'{<}^{H}_{OH}$ and its reciprocal $H_2O{<}^{R'}_{X'}$ under the influence of the electromotive force; electrolysis only takes place when both the hydrol and its reciprocal are present.

The proportion of hydrol is presumably at a minimum in concentrated solutions, that of its reciprocal at a maximum: in other words, water is in its most active state in solutions in which there is a maximum proportion of the solute, in the sense that it is the most active in conditioning "hydrolysis" of molecules of the solute. In dilute solutions, which contain the maximum proportion of hydrolated substance, the molecules of the solute have the greater opportunity of becoming hydrolated and of remaining hydrolated both because they are present in small number and because the water contains the minimum proportion of hydrone or hydronol: hydrolated molecules are therefore less subject to dehydrolation.

When a substance such as hydrogen chloride is dissolved in water, it is to be supposed that it enters into solution as the simple or fundamental molecule and that the changes that attend alterations in concentration are "hydration" changes. As the concentration is diminished, change must take place more and more in the direction pictured by the expression—

$$H_2O{<}^{H}_{Cl} \rightarrow HCl{<}^{H}_{OH}$$

but there is no reason to assume that ultimately the whole is converted into the hydrol HCl:H(OH); probably a certain proportion becomes hydronated.

In the case of salts indeed, of all substances that enter into solution in a more or less polymerised condition, more or less complete depolymerisation is effected as the dissociating influence of the solvent is increased by an increase in its amount. Ostwald's dilution law is probably the expression of depolymerisation changes such as are here pictured.

As molecular electrolytic conductivity is at a maximum in dilute aqueous solutions, a preponderating influence in electrolysis may be ascribed to the hydrols—although these cannot act alone. Chemical activity, on the other hand, is often, if not always, at a maximum in more or less concentrated solutions; in such cases, apparently, the reciprocal of the hydrol—the compound $H_2O{<}^{R'}_{X'}$—exercises the preponderating influence.

From the point of view here advocated, the term acid acquires a somewhat special meaning. As everyone knows, the name oxygen was given by Lavoisier to the active constituent of the atmosphere because he supposed it to be the determining cause of acidity. It is now customary to assert that the proof given by Davy that "muriatic acid" does not contain oxygen was the death-blow to the Lavoisierian conception. So long as dualistic views were in vogue, it was customary to speak of salts as composed of acid and base; the non-metallic oxide was thought of as the acid; this practice survives to the present day in the frequent use of the name carbonic acid for the higher oxide of carbon. The late Professor Williamson never ceased to advocate the use of sulphuric acid as the name of sulphur trioxide; he consistently termed what is now commonly spoken of as sulphuric acid, hydric sulphate. Manufacturers of sulphuric acid still speak of "monohydrate" when referring to the compound formulated as H_2SO_4. Moreover, those who belong to the electrolytic dissociation school do not think of this compound as *the acid*—the acidic properties arise only when it is dissolved in water and is thereby resolved into its ions; the attribute "acidity" is associated with the hydrogen ion, not with the compound as a whole.

If water play the part I have suggested, *the acid* is formed from water and the substance the presence of which confers acidic properties upon the solution; the term acid should therefore be restricted to the product thus formed with the assistance of water. Throughout these communications, I have advisedly spoken of and drawn a distinction between hydrogen chloride and chlorhydric acid—meaning by the former the compound represented by the formula ClH, by the latter the product present in an aqueous solution of this compound. In any case, the term hydrochloric acid is a misnomer—the substance has connexion neither with water, as suggested by the prefix hydro, nor with chloric acid, as suggested by the suffix; and it is not an acid by itself. Why should we go beyond the name hydrogen chloride? No other could possibly be so significant: it tells us exactly what we know of the compound; hydrochloric acid tells us nothing that we know of it.

The argument may be applied to acids generally. I prefer to speak of hydric nitrate and hydric sulphate—following Frankland and Williamson—and to apply the terms nitric and sulphuric acids to the compounds formed from them and water. A term such as hydric nitrate is of value as connotative of the survival of an element of water in the compound.

One other remark: the view I have taken throughout this communication, if accepted, is one that restores to its full significance Lavoisier's conception of oxygen as *the*

acid-forming element; if I am right, oxygen *is* a constituent of all recognised acids and the constituent to which they owe their special activity.

This is probably true of all compounds that dissolve in water and in so doing acquire activity. Thus the interaction of acid and alkali may be pictured as primarily that of two hydrolated compounds, for example:

$$HCl{<}^{H}_{OH} + {}^{HO}_{H}{>}ONaH = NaCl + 2H_2O.$$

The amount of water actually formed by this interaction and the consequent expansion (compare VI and XVI) is determined by the proportion in which the two compounds are present as hydrols in the solutions used and the extent to which the salt becomes hydrolated. Strong acids are those which are hydrolated to a considerable extent, weak acids those which are but slightly hydrolated. From this point of view, it is not difficult to understand that the heats of neutralisation of different strong acids or bases should be so nearly equal, the heat evolved being chiefly due to the liberation of hydrone and its conversion into water (compare Pickering, *Trans.*, 1887, li., 593).

Hydrolytic changes should also be pictured as cases in which hydrolyst and hydrolyte are brought initially into association through their hydrols, just as are acid and alkali. In this connexion, again, distinction should be drawn according as the interacting substances are more or less hydrolated; in other words, it must be recognised that there are both strong and weak hydrolytes. Hydrolytes such as methylic acetate apparently are to be reckoned among the latter (compare VIII, p. 109).

When the influence exerted by non-electrolytes on electrical conductivity, on solubility and on hydrolytic activity is considered (I, II, VIII, XI, XIII, XVIII), it is clear that a broad division may be made into compounds which have a marked affinity for water and those which have but slight affinity. The sugars may be taken as typical of the one class; the higher monohydric alcohols as typical of the other. The former in many cases *appear* to exercise little influence; in other cases, they promote rather than retard change: thus they tend to increase rather than diminish solubility - such an effect may, with some show of reason, be attributed to a superior solvent action exercised at their hydrolated surfaces. Non-electrolytes which have little attraction for water not only have no such effect but, owing to their comparative freedom in the solution, are able to interfere mechanically and thereby more or less diminish the extent to which the compounds with which they are mixed become hydrolated. This effect, which appears to be exercised very generally and is probably of great importance, is one that has attracted but little attention.

The several conclusions thus arrived at are summarised in a single sentence when it is stated that, in all cases of chemical activity displayed by substances in aqueous solutions, the change that takes place is initially one in which hydrolated molecules of the interacting substances are concerned, strength and weakness corresponding respectively to high and low proportions of hydrolated molecules.

Of late years, the properties of water, regarded from a chemical point of view, have been left out of account to an extraordinary extent by most of those who have studied solutions; it is essential, however, that while using physical methods we should consider the results in the light of our experience as chemists: this is our first duty. As the inquiry to which this communication relates has been extended, the conviction has been more and more forced upon me and upon my co-workers that the phenomena represented by solutions are of infinite complexity. We are persuaded that it is impossible, as a rule, to interpret them in the absolute manner customary of late years; we even doubt the possibility of submitting them to any simple form of analytical treatment.

The further series of communications now submitted, XII—XVIII, only serve to confirm this opinion.

Addendum.

Electrolysis of Non-aqueous Electrolytes.

The fundamental distinction I have drawn between compounds which are potentially electrolytes and those which are not is that when dissolved in water, in the case of the one but not in that of the other, solvent and solute are both *reciprocally distributed*; moreover, I also assume that the two products are *reciprocally concerned in the operation which constitutes electrolysis*. I will now venture to make the further suggestion that the electrolysis of fused and dissolved salts may be interpreted in a similar manner. Relatively few salts are electrolytes—the salts of silver, those of the alkali metals and those of the alkaline-earth metals and allied elements such as lead and stannous tin are all decomposed by an electric current; but that most enigmatic of all chlorides, mercuric chloride, also stannic chloride and per-salts generally as well as many if not all salts of metals of higher valency than the dyads seem not to be affected by the current unless mixed with others.

If electrolysis be an interdependent process in the case of salts as in the case of solutions, the differences in the behaviour of salts must have their origin in some fundamental difference in the character of the salts. When comparison is made between hydrogen chloride and common salt, for example, it is clear that the ideal compound formulated as NaCl is to be regarded as an eminently unsaturated substance—"unsaturated," that is to say towards itself as well as towards water, whilst hydrogen chloride in no way behaves as if it were unsaturated towards itself although it is obviously unsaturated towards water, &c.; assuming that the activity of sodium chloride is conditioned by the chlorine radicle, it follows that the sodium atom has a relatively slight power of neutralising the halogen and that the two radicles may have relatively slight affinity for each other. The fixity of salt, on this assumption, it may be pointed out, may well be a consequence of the high degree of residual affinity of chlorine atoms and their intense inter-affinity when associated with sodium atoms. The volatility of a compound such as mercuric chloride, on the other hand, may be regarded as proof that the chlorine atoms are all but neutralised by the metallic atom or, if not by this alone, by their own interconnexion as well; a similar view may be taken of per-salts generally.

The difference between the two classes of salts is of somewhat the same order as the difference which obtains between water and alcohol: if the assumption be made that in the one case but not in the other the molecules may become "distributed" among themselves, an explanation is afforded of the fact that salts of the one class (in the fused or viscous state) are electrolytes, whilst those of the other class are not—that in the case of common salt, for example, the liquid contains the forms—

$$(NaCl)_x \qquad NaCl \qquad NaCl{<}^{Cl}_{Cl} \qquad NaCl{<}^{Na}_{Na}$$

Walden's refined and comprehensive studies furnish most important evidence that solvents other than water are incapable of producing effects such as water produces.

Water regarded as a solute is no exception to the rule that "volatile" binary compounds are not electrolytes, being not only a non-conductor itself but remaining inert even when dissolved in solvents of high specific conductive capacity such as hydrogen cyanide.

The substances which behave as electrolytes when dissolved in "neutral" solvents, as a rule, are substances which are conductors in the fused state: in their case, it may be supposed, dissolution is equivalent to fusion.

The invaluable observations by Wallace Walker, McIntosh and Archibald (*Trans. Chem. Soc.*, 1904, 1082—1105) and by Steele and these two latter workers (*Trans. Roy. Soc.*, 1906, A, ccv., 99) have shown that certain solvents, notably the halogen hydrides, are not neutral. In such cases, as the authors mentioned point out, compounds of the two substances (of solvent with solute) are formed which are themselves electrolytes and behave as salts, in fact.

It is a striking circumstance that whereas a solution of hydrogen cyanide in water is practically without conducting power, the corresponding solution of hydrogen cyanide in hydrogen chloride is a moderate conductor—and that in the one case, intermixture is attended with but a slight development of heat, whilst in the other much heat is given out. Compounds such as that which is formed from hydrogen cyanide and hydrogen chloride are obviously comparable with ammonium chloride and their behaviour as electrolytes may be accounted for on the assumption that in the liquid state they exist in reciprocal forms. In the case of hydrogen chloride, assuming that the interaction takes place in accordance with the equation—

$$\underset{\text{Methinylamine.}}{HC{:}N} + HCl = \underset{\substack{\text{Methinylammonium}\\ \text{chloride.}}}{HC{:}NH.Cl}$$

the two forms would be—

$$(HC{:}NH)\cdot Cl\lessdot^{Cl}_{Cl} \quad \text{and} \quad (HC{:}NH)\cdot Cl\lessdot^{(NH{:}HC)}_{(NH{:}HC)}$$

We are thus brought back to the conclusion formulated originally by Hittorf that in all cases: *Elektrolyte sind Salze*—but only some salts.

The distinction between water and other "active" solvents would appear to be that in the case of water the molecules of the solvent as well as those of the solute become distributed; whilst in the case of solvents other than water the molecules of the compound that is formed from solvent and solute become distributed among themselves; hence the great difference between water and other solvents. *The properties of water seem to be singular in all respects.*

It has been assumed of late years that both "ions" are hydrated in aqueous solutions—the suggestions that I have put forward involve the assumption that the negative radicle alone becomes hydrated. Attempts have been made to determine the extent to which the two ions are hydrated by determining the changes in concentration at the two electrodes relatively to a neutral substance which, it is assumed, does not wander. Washburn, for example, has used raffinose for this purpose; but if the water in a solution wander during electrolysis, any and every substance in the solution must wander with the water. The hydrogen radicle, I would suggest, can only be regarded as an absolute monad—its mobility is presumably an expression of this property.

CAPSAICIN, THE PUNGENT PRINCIPLE OF CAPSICUM, AND THE DETECTION OF CAPSICUM.

By E. K. NELSON.

Thresh, in 1876, established the fact that a crystalline powerfully pungent principle, which he named capsaicin, is the main active body in capsicum (*Pharm. Journ. and Trans.*, iii., 7, 21, 259, 473).

Morbitz isolated a principle from capsicum which he termed "capsacutin" (*Pharm. Zeit. f. Russland*, 1897, p. 369), but Micko (*Zeit. f. Unters. d. N. u. Genussm.*, 1898, p. 818), who has done the most recent work on the subject, showed that the body isolated by Morbitz is identical with the capsaicin of Thresh, being probably an impure form of the latter body.

Micko developed a process for the isolation of capsaicin, and proved it to be the pungent principle of pepper (Capsicum fastigiatum), but that Capsicum fastigiatum contains about twenty times as much capsaicin as does Capsicum annuum (*Ibid.*, 1899, p. 411).

In view of the fact that the detection of capsicum is desirable in most cases where it is used to fortify pungent beverages, such as ginger ale, it seemed desirable to isolate some of the pure principle for the purpose of studying some of its properties.

The method of Micko was employed, and while extremely tedious and difficult, it is apparently the only way at present known whereby the body can be satisfactorily separated from the fatty and resinous bodies with which it is associated.

Fifteen hundred grms. of ground African cayenne were completely exhausted with ether. The ether was distilled off, and the residue, a red very pungent oil, was dissolved in 1 litre of 90 per cent alcohol, made slightly alkaline with alcoholic potash, and well agitated. A portion of the oil remained undissolved. This was separated, agitated with 90 per cent alcohol, and the alcoholic solutions, which contained the pungent principle, were united. Barium chloride solution was added to the alcoholic solution in moderate excess, and the mixture was thoroughly agitated. After standing for several hours, the clear liquid was decanted from the precipitate, and the latter was washed with alcohol on a glass-wool filter.

The alcohol from the alcoholic solution was removed by distillation, and the residue was agitated with warm water. On standing, an oil separated, which was removed, and the aqueous layer was shaken out with chloroform, the residue from which was united with the main portion of oil. The oil was taken up with 90 per cent alcohol, exactly neutralised with alcoholic potash, and sufficient alcohol added to bring the volume to 2 litres. Alcoholic solution of silver nitrate was then added, while stirring, in moderate excess. A brownish red, very voluminous precipitate was thrown down which was filtered off, and washed with alcohol until the pungent principle was completely removed.

From the filtrate silver nitrate was removed by adding sodium chloride in aqueous solution, and filtering. The alcohol was distilled from the filtrate, the residue mixed with water, and the oil separated. This oily material was then dissolved with an excess of 5 per cent potassium hydrate solution, and carbon dioxide passed into the solution until it was completely saturated with that gas.

This caused the separation of an oily layer which was removed by shaking out with ether. The residue from the ether was put into an 8-litre flask, mixed with 100 cc. of 5 per cent potassium hydrate, diluted with 3 litres of water, heated to 60°, and allowed to stand overnight at room temperature. The alkaline, slightly coloured, clear solution was syphoned from the oily insoluble material left adhering to the walls of the flask.

The above process was repeated until pungent bodies were completely removed from the residue. The alkaline clear solutions thus obtained were united in a large flask, heated to 60°, and barium chloride solution, in sufficient excess, was added, while stirring.

On standing, the precipitate settled out, and the clear supernatant liquor was removed. The precipitate was repeatedly treated with potassium hydrate solution, and subsequent precipitation with barium chloride until it was free from pungent bodies. The clear filtered solutions from the barium precipitate were acidified (whereupon they became milky) and shaken out with chloroform.

The chloroform was evaporated, and after standing for some days the residue began to crystallise in rosettes, and set finally to a solid beautifully crystalline mass. The crystalline material had a brownish yellow colour, and was contaminated with some oily material. It was spread on a porous plate, and the oil and much of the colour absorbed. The crude crystals were dissolved in carbon bisulphide, a gummy residue remaining undissolved.

The carbon bisulphide was evaporated in a flask, and the residue boiled out with petroleum ether under a reflux condenser, decanting the petroleum ether extracts into beakers.

Upon cooling, pearly leaflets separated from the petroleum ether solutions.

The body thus obtained was perfectly pure capsaicin, in the form of pearly white leaflets.

All residue and liquors were carefully examined for other bodies of a pungent nature with negative results. Hence,

is concluded that capsaicin is the only pungent principle of capsicum. An alkaloidal substance, capsicin, possessing a conin-like odour, is present in minute amount, but it is not pungent.

From 1500 grms. of selected African pods (Capsicum fastigiatum), 2·13 grms. of pure crystalline capsaicin were obtained, representing 0·14 per cent of the original material. The crystals melt at 64·5° (Micko's capsaicin melted at 64°). The properties of the bodies agree well with those described by Micko.

Capsaicin is not an alkaloidal body, but possesses some of the properties of the phenol group. Micko has shown that it contains a methoxy group and a hydroxyl group, and from analysis and molecular weight determinations ascribes to it the formula $C_{18}H_{28}NO_3$. The enormous pungency of capsaicin can be appreciated only by those who have been brought intimately in contact with it. One drop of a solution containing 1 part in 100,000 causes a persistent burning on the tongue. A drop of a solution of 1 part to a million imparts a perceptible warmth.

Now one drop of a solution of one part per million contains at the most 1/20,000 of a mgrm. of capsaicin, an amount not only unweighable, but extremely difficult of detection even by the most delicate of chemical reagents. The only test based on chemical reaction indicating capsaicin on record, to the writer's knowledge, is that described by Micko, (*Zeit. f. Unters. d. Narhr. u. Genussm.*, 1898, p. 818), and is as follows:—An alcoholic solution of capsaicin acidulated with hydrochloric acid is treated with an excess of platinic chloride; no precipitate is formed. On spontaneous evaporation of this mixture, however, a characteristic vanilla-like odour is developed after some time.

To test the delicacy of this reaction, weighed amounts of capsaicin in alcoholic solution were treated with platinic chloride and hydrochloric acid, as directed, with the following resufts:—

4/10 mgrms. gave no odour.
2 mgrms. gave a slight odour which could not be described as the odour of vanilla.
4 mgrms. gave a slight vanilla odour.
10 mgrms. gave a distinct vanilla odour.

Thus it seems that this method, depending on the sense of smell, is entirely valueless for the detection of small amounts of capsicum. Careful search was made for a micro-chemical reaction which could be utilised for the detection of small amounts of capsaicin, but none was found.

The following test indicates the presence of capsaicin:—On treating a small amount of capsaicin with a dilute neutral solution of ferric chloride and a little alcohol, an evanescent greenish blue colour is given. This reaction is neither characteristic nor delicate, and is therefore of no value for analytical purposes.

When capsaicin is dissolved in sulphuric acid and a particle of sugar added, a beautiful violet colour develops on standing, a reaction, however, which is afforded by other substances.

The detection of small amounts of capsicum therefore appears to be restricted to the physiological action of the capsaicin.

Garnett and Grier (*Pharm. Journ. and Trans.*, [3], xii., 721) were the first to describe a method for the detection of capsicum in ginger preparations, based on this reaction. The pungent body of ginger (gingerol) is destroyed by them by heating on the water-bath with alcohol potassium hydrate.

The pungent substance of ginger is not, however, completely destroyed by this method, as can readily be observed by the very perceptible burning taste left after treating tincture of ginger by their method. Furthermore, the residue obtained according to this method is quite considersiderable, as ether is used for the extraction, and it dissolves the oleo-resins of ginger, thus diluting the pungent body in the residue and rendering the test less delicate.

A method is here proposed which departs from the Garnett and Grier method in important particulars, and which is described as follows:—

Ten cc. of a tincture, or the ether extract from 100 cc. of a beverage (from which any alcohol present has been evaporated previous to extraction with ether) are treated in a porcelain dish with 10 cc. double normal alcoholic potassium hydroxide and evaporated on the steam-bath.

About one-tenth grain powdered manganese dioxide is added, 5 to 10 cc. water, and the heating on the bath continued for about twenty minutes, or until volatile oils are expelled. Cool, acidify with dilute sulphuric acid, and extract at once with petroleum ether. Evaporate the petroleum ether in a small crucible, keeping the residue within as small an area as possible, and heating on the steam-bath for about five minutes. The residue will be very small and in some cases scarcely visible, and it will contain all the capsaicin from capsicum, mixed with a minimum amount of extractive matter. Apply the tongue to the residue, being careful to keep the material on the tip of the tongue. If capsicum is present the characteristic burning sensation will soon be felt.

If but a minute amount of capsicum is present, it may take a few minutes for the reaction to develop. In some cases it may be necessary to apply the entire residue to the tongue.

From the nature of the substance it is desirable to allow an interval of time between the several testings. Failure to follow this course may result in confusion.

The following data will show the delicacy of the test where capsicum in small amount is mixed with ginger:—

Tr. ginger	U.S.P.	10 cc.	No capsicum found.
Tr. capsicum	U.S.P.	None.	
Tr. ginger	U.S.P.	10 cc.	Capsicum detected by placing entire residue on tongue.
Tr. capsicum	U.S.P.	1/100 cc.	
Tr. ginger	U.S.P.	10 cc.	Capsicum taste very pronounced.
Tr. capsicum	U.S.P.	1/10 cc.	
Tr. ginger	U.S.P.	10 cc.	Capsicum taste extremely hot.
Tr. capsicum	U.S.P.	5/10 cc.	

—*Journal of Industrial and Engineering Chemistry*, ii., No. 10.

Royal Institution.—The following are the lecture arrangements at the Royal Institution after Easter:—Mr. J. E. C. Bodley, three lectures on—(1) "Cardinal Manning"; (2) "The Decay of Idealism in France, and of Tradition in England"; (3) "The Institute of France"; Prof. F. W. Mott, two lectures on "The Brain and the Hand"; Prof. W. W. Watts, two lectures on—(1) "The Ancient Volcano of Charnwood Forest (Leicestershire)"; (2) "Charnwood Forest and its Fossil Landscape"; Prof. R. W. Wood, of the Johns Hopkins University, three lectures on the "Optical Properties of Metallic Vapours" (illustrated); Dr. W. N. Shaw, two lectures on Air and the Flying Machine—(1) "The Structure of the Atmosphere and the Texture of Air Currents"; (2) "Conditions of Safety for Floaters and Fliers"; Mr. T. Thorne-Baker, two lectures on (1) "Changes effected by Light"; (2) "Practical Progress in Wireless Telegraphy" (illustrated); Prof. Selwyn Image, three lectures on—(1) "John Ruskin; or, the Seer and Art"; (2) "William Morris; or, the Craftsman and Art"; (3) "Walter Pater; or, the Connoisseur and Art"; Mr. W. P. Pycraft, two lectures on "Phases of Bird Life: (1) Flight; (2) Migration"; and Mr. W. L. Courtney, two lectures on "Types of Greek Women—Nausicaa and the Homeric Women; Sappho and the Æolian Poets; Aspasia and Pericles." The Friday Evening Meetings will be resumed on April 28, when a Discourse will be given by Prof. W. M. Flinders Petrie on "The Revolutions of Civilisation." Succeeding Discourses will probably be given by Prof. M. O. Forster, Prof. W. Stirling, Prof. R. W. Wood, Prof. G. Murray, Commendatore G. Marconi, Prof. Svante Arrhenius, and other gentlemen.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 16th, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Constitution of the Alloys of Aluminium and Zinc.*" By Walter Rosenhain and Sydney L. Archbutt.

In connection with researches on light alloys, carried out on behalf of the Alloys Research Committee of the Institution of Mechanical Engineers, the authors have studied the constitution of the Al-Zn alloys by pyrometric and microscopic methods, including the study of specimens after prolonged annealing at definite temperatures and after quenching. The results are represented in an equilibrium diagram differing materially from those previously put forward. The principal points of difference are:—

1. The liquidus curve shows a small break at a concentration of 85 per cent of zinc, this break being connected with the formation of a definite compound of probable formula Al_2Zn_3.

2. In alloys under conditions of complete equilibrium the occurrence of eutectic ceases at a concentration of about 78 per cent of zinc, although in ordinary slowly-cooled alloys the eutectic can be traced down to the vicinity of 50 per cent zinc.

3. At a concentration of about 78 per cent of zinc, the solidus curve of the alloys rises abruptly from the eutectic line (380° C.) to a horizontal line of arrest-points at 443° C. This line commences at the break in the liquidus curve already mentioned, and extends to about 37 per cent of zinc; between 78 and 40 per cent this line represents the solidus, but near 40 per cent the solidus bends upwards towards the melting-point of pure aluminium. The reaction indicated by this line of arrest-points is the formation of a compound (Al_2Zn_3) by the reaction of crystals of a solid solution of zinc in aluminium with the residual liquid.

4. A second horizontal line of arrest-points of considerable intensity has been found at 256° C. in alloys containing 99 to 35 per cent of zinc. These heat evolutions are due to decomposition of the compound (Al_2Zn_3) into two phases, one of which is the saturated solid solution of Zn in Al, while the other is practically pure Zn.

5. The existence of a definite compound is indicated, stable only between 443° C. and 256° C., and having a zinc content of about 78 per cent, most nearly represented by Al_2Zn_3. Evidence for its existence is derived from the termination of the eutectic line and the position of maximum intensity of the line of heat evolutions just mentioned; this is strikingly confirmed by the micro-structures, which show the compound in the form of characteristic hexagonal dendrites. When decomposed (at or below 256° C.), it exhibits a duplex laminated "pearlitic" structure strikingly resembling the pearlite of carbon steel.

"*Production and Properties of Soft Röntgen Radiation.*" By R. Whiddington, B.A.

Röntgen rays from ordinary bulbs are usually produced at generating potentials of between 10,000 and 100,000 volts. It is possible by using a special tube with a very thin aluminium window to experiment with rays generated at only a few hundred volts. The rays dealt with in this paper were generated at 1000 to 3600 volts.

It has been found that such soft Röntgen rays have much the same properties as the harder rays usually experimented with. They produce ionisation in air, affect photographic plates, and can excite secondary radiations when incident on solid bodies. Their range in air, however, is not many centimetres.

For many purposes a Röntgen radiation is sufficiently defined by a knowledge of—(1) the total energy; (2) the penetrating powers in absorbing screens. These two properties have therefore been investigated in some detail, with reference particularly to the influence exerted by—(1) the material of the anticathode; (2) the potential at which the rays were generated.

The anticathodes used fall naturally into two groupings:—Group A: Al, Pt. Group B: Ag, Cd, Cu, Fe, Ni, Pb, Sb, Sn, Zn.

The anticathodes of Group A emit secondary radiations; those of Group B do not. Experiment indicates that Al emits a soft characteristic radiation of λ/ρ 580 (in Al). In order to arrive at a common explanation of a number of experimental results it is suggested that this Al radiation disobeys the law of "Röntgen Ray Fluorescence" recently advanced by Barkla.

"*Experiments on Stream-line Motion in Curved Pipes.*" By Prof. J. Eustice, B.Sc.

In a paper on the "Flow of Water in Curved Pipes," the author has shown that during the flow of water through a pipe, if a change is made from a straight to a very slightly curved form there is an increased resistance to flow which is very marked at velocities below the critical velocity.

In order to find the cause of the increase in resistance an apparatus was designed which provides for the distribution of six variously coloured filaments of dyed water into a glass pipe through which water is flowing. The positions of the filaments can be so arranged that in the passage of water from a straight to a curved pipe the directions of the stream-lines in any part of the tube can be investigated.

The experiments show that the curvature of a filament is less than the curvature of that part of the pipe in which the filament is flowing, and if the velocity of flow increases the curvature of the filament increases. The filaments impinge on the outer wall of the pipe, and, flattening into bands, follow the surface of the pipe and cross over to the inner wall, where the filaments start again in their path along the main stream, until (if the pipe is sufficiently long) the filaments again meet the outer wall, when the return flow along the surface is repeated.

A filament flowing in the central plane of the pipe, when reaching the outer wall, divides into two parts which come together on the inner wall of the pipe; the other filaments flow through the loop which is thus formed. A filament not in the central plane remains on that side of the plane in which it enters the curved pipe.

The experiments were extended to angle pipes, and the velocities were increased until turbulent motion was obtained. After flowing through a curved pipe or angle, vortices are generated which persist in a contiguous straight pipe.

CHEMICAL SOCIETY.

Ordinary Meeting, February 16th, 1911.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. S. Judd Lewis and Walter N. Haworth were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Samuel James Manson Auld, D.Sc., Ph.D., 65, Margery Park Road, Forest Gate, E.; Arthur Stewart Bowyer, M.Sc., The Woodlands, Chelford; Cecil Reginald Crymble, B.Sc., 7, Upper Crescent, Belfast; Oliver Statham Douse, B.Sc., Fern Bank, Glossop; Alfred Henry Finniss-Wheldon, 446, Currie Road, Durban, Natal, S. Africa; Henry Francis Harwood, M.Sc., Ph.D., Erlesdene, Park Road, Hale; Thomas Riley Lucas, No. 3 Cantonments, Vizianagram, Madras, India; Roney Forshaw Messervy, 73, Blenheim Crescent, W.; John Lawrence Robinson Pastfield, B.A., Olivevale, St. Thomas, Exeter; Richard Garnet Penney, 40, Duesbery Street, Hull; Robert Wright, M.A., Lauriston, Derryvolgie Avenue, Belfast.

The President announced that the Council had recom-

mended the following gentlemen as Honorary and Foreign Members, and that a ballot for their election would be held at the next Ordinary Scientific Meeting of the Society :—Prof. Dr. Eugen Bamberger (Zürich), Prof. Giacomo Ciamician (Bologna), Prof. Dr. Paul Heinrich Ritter von Groth (Munich), Prof John William Mallet (Virginia), Prof. Dr. Walther Nernst (Berlin).

It was stated that the following changes in the Officers and Council were proposed by the Council :—

President to retire—Prof. H. B. Dixon.

Vice-Presidents to retire—Dr. J. J. Dobbie and Prof. F. S. Kipping.

Ordinary Members of Council to retire—Mr. J. L. Baker, Dr. G. T. Beilby, Dr. J. T. Hewitt, and Dr. H. R. Le Sueur.

As President—Prof. Percy F Frankland.

As Vice-Presidents who have filled the office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. H. B. Dixon, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Sir William Ramsay, Prof. J. Emerson Reynolds, The Right Hon. Sir Henry E. Roscoe, Sir Edward Thorpe, and Sir William Tilden.

As Treasurer—Dr. Alexander Scott.

As Hon. Secretaries—Prof. Arthur W. Crossley and Dr. G. T. Morgan.

As Foreign Secretary—Dr. Horace T. Brown.

As Vice-Presidents—Dr. G. T. Beilby, Dr. J. N. Collie, Dr. M. O. Forster, Prof. A. Liversidge, Prof. W. J. Pope, and Prof. J. Walker.

As New Ordinary Members of Council—Mr. W. R. Bousfield, Mr. C. F. Cross, Mr. A. R. Ling, and Dr. H. Marshall.

Dr. V. H. Veley, Dr. F. B. Power, and Prof. J. Millar Thomson were elected Auditors to audit the Society's accounts.

The PRESIDENT announced that Mr. G. H. Gabb had presented to the Society a portrait of Dr. John Jeffries, from the pastel by John Russell, R. A.

A ballot for the election of Fellows was held, and the following were subsequently declared elected :—Solomon Farley Acree ; James Allan, M.A., B.Sc. ; Edward Anderson ; Albert Ashe ; John Ewart Trounce Barbary ; Joseph Bate ; Joseph Mayson Blackburn ; Walter Norman Burbridge ; John Fisher Carmichael, B.Sc. ; Harold Christopher, B.Sc. ; Morris Cutner, B.Sc. ; James Edward A. Devlin ; Harold Edgar Dryden ; James Furnival Eardley ; Robert Leonard Emerson, A.B., M.D. ; Michael Angelo Fielding ; William Temple Gardner ; Evan Dalton Griffiths, B.Sc. ; Arthur Bennett Hall ; Charles Herbert Hampshire, B.Sc. ; Henry George Alan Harding ; William Joseph Chetwynd Horne ; Bernard Grindrod Hough ; Reginald Hurst ; William Alfred Jenkin ; Ernyst Graham Laws, B.A. ; James William McBain, M.A., Ph.D. ; John Watterson Miller ; Walter Roman Moore ; Harold James Page ; Edward Partington ; Cyril James Peddle, M.Sc. ; Frank Henry Plews ; Henry Stanley Raper ; Robert Viner Stanford, M.Sc., Ph.D. ; George Douglas Summers ; David Thomson, M.A., B.Sc., Ph.D. ; William Denham Verchoyle ; Bertie James Waygood ; Ian Gordon Sellar Wink ; Edward Escott Wood ; Charles Fursdon Yates.

Of the following papers, those marked * were read :—

*40. "*Different Methods of Applying the Grignard Reagents.*" By HAROLD DAVIES and FREDERIC STANLEY KIPPING.

Attention was drawn to the fact that in many of the syntheses which involve the use of a Grignard compound, the preliminary preparation of an ethereal solution of this reagent is quite unnecessary, because the desired result may be attained by Barbier's method. It was shown by examples that tertiary alcohols may be obtained by mixing a ketone (not acetone, however) or an ester with an alkyl or aryl halogen compound, and then adding the mixture to magnesium in presence of ether ; the formation of hydrocarbons (diphenyl, dibenzyl) as by-products, which is often a source of much trouble in using the magnesium aryl halogen compounds, is thus avoided. The method has been previously adopted in preparing certain silicon compounds (*Trans.*, 1908, xciii., 2006 ; 1909, xcv., 306), and, as was shown, may also be employed in the synthesis of alkyl derivatives of tin.

DISCUSSION.

Dr. ALEX. MCKENZIE referred to the preparation of the Grignard reagent from an aryl halide in the ordinary manner, when the main reaction is accompanied by the secondary reaction, $XR + RMgX = R{\cdot}R + MgX_2$; thus diphenyl was formed during the preparation of magnesium phenyl bromide. Such hydrocarbons were not always readily separated from the reaction products, but the extent of their formation might be lessened by the device suggested by Schmidlin, who recommended the use of an excess of magnesium amounting to from twice to thrice the calculated quantity.

*41. "*Molecular Association and its Relationship to Electrolytic Dissociation. The Molecular Complexity of Halogen-containing Compounds.*" By WILLIAM ERNEST STEPHEN TURNER.

The investigation was undertaken with the object of defining the conditions under which molecular association of halogen containing compounds takes place, and to test whether such association could be attributed to the possession by the halogen atom of latent or residual valencies. The experimental work involved the examination, in indifferent solvents of about sixty different substances, and information concerning other substances was collected from different sources. More than a hundred substances of different types, including salts, were inspected in the complete review.

The question of the molecular complexity of salts was approached through the halogen salts of organic nitrogen, oxygen, and sulphur bases, many of these salts being found soluble in chloroform. The information then obtained was applied to the metallic salts. The chief conclusions were :—

1. Molecular association of chlorine-containing compounds only occurs when the compound is electrically active ; that is, is either an electrolyte or a conducting medium.

2. The degree of association in chloroform of the salts of organic bases is very high, the association factors ranging in different salts from about 1·5 to 12, in solutions which seldom exceed 10 per cent. Chlorides were always least, and iodides most associated. When salts of similar bases are compared, the degree of association decreases with the mass of the base.

3. With metallic salts, the iodides are least associated, and chlorides most. In salts derived from allied metals, the degree of association decreases with increase of the atomic weight, and increases with the electro-positive character of the metal.

4. Molecular association is the complement of electrolytic dissociation. Substances dissociated in ionising media are associated in different solvents.

5. Latent valencies do not give rise to association, at least directly. It is better to view association in connection with the electrical properties of the substance.

DISCUSSION.

Sir W. RAMSAY drew attention to the fact that possibly chloroform as a solvent might exert "latent valencies," or "residual valencies," due to the possibility of chlorine acting not merely as a monad, but as a triad.

He also added that the main objection to the idea of "molecular compounds" was that molecules, as such, could not conduct ; that molecules did not act as carriers of electricity ; that property belonged exclusively to ions. Hence valency must be a property of ions, not of molecules, if there was any truth in the hypothesis that valency is due to the transit of electrons from one atom to another.

Dr. PHILIP drew attention to the fact that the molecular

weight of ethyl alcohol in benzene, calculated from cryoscopic observations on 12 to 15 per cent solutions, was four or five times the normal value, whereas the association factor of pure ethyl alcohol was about 3. He asked if Dr. Turner could offer any explanation of this difficulty.

Mr. Turner stated, in reply to Sir William Ramsay, that the possible combination of solvent and solute had been considered, but no evidence had been obtained during the investigation that such combination occurred. Moreover, in all cases, so far as the author was aware, combination between solvent and solute resulted, not in raising but in *lowering* the molecular-weight values.

In reply to Dr. Barger, he considered that the use of pyridine as a solvent in the determination of molecular weights was objectionable for two reasons. It had a fairly high dielectric constant, and it combined with the solute.

With reference to Dr. Philip's question, the author could offer no plausible suggestion why alcohol should be so much more associated in benzene solution than in the liquid state.

In reply to Dr. Senter, Mr. Turner stated that the molecular complexities quoted of the haloid salts of the alkali metals were calculated by Walden by means of a formula which was free from the objections raised against the original Ramsay and Shields' formula. The results were also in accord with values obtained by a second method not involving a measurement of surface tension.

42. "*α*-p-*Hydroxy*-m-*methoxyphenylethylamine, and the Resolution of α* p-*Hydroxyphenylethylamine*." By Charles Watson Moore.

The author has prepared α-p-*hydroxy*-m-*methoxyphenylethylamine* by the reduction of 4-hydroxy-3-methoxyacetophenoneoxime. The base is found to have a slight action on the blood pressure. The *hydrochloride* and the *benzoyl* derivatives have also been prepared and characterised.

α-p-Hydroxyphenylethylamine was prepared by Tutin, Caton, and Hann (*Trans.*, 1909, xcv., 2113), and was shown (*loc. cit.*) to exert an action on the blood pressure similar to, although much less than, epinephrine. Since the base contains an asymmetric carbon atom, it was considered of interest to ascertain whether the optically active bases, obtained by its resolution, would differ in physiological activity, as in the case of the *d*- and *l*-epinephrines (Cushny, *Pharm. Journ.*, 1909, lxxxii., 56), and the *d*- and *l*-hyoscyamines (Cushny, *Journ. Physiol.*, 1904, xxx., 176). The base had been resolved by means of its d-*camphorsulphonate*, although only the salt of the lævorotatory base has been obtained in a pure condition. Optically pure benzoyl derivatives have, however, been obtained from both the stereoisomeric bases. The effect on the blood pressure of the *l*- and *dl*-bases has been determined, but no difference in physiological activity was observed.

43. "*The Formation and Reactions of Imino-compounds.* Part XV. *The Production of Imino-derivativez of Piperidine leading to the Formation of the ββ Disubstituted Glutaric Acids.*" By Ferdinand Bernard Thole and Jocelyn Field Thorpe.

It was shown that almost quantitative yields of the ββ-disubstituted glutaric acids can be obtained by condensing cyanoacetamide with ketones in the presence of piperidine or alkali hydroxide. The imino-piperidones which are initially formed decompose under the action of strong acids, yielding the substituted glutaric acids (compare *Proc.*, 1910, xxvi., 295).

44. "*The Interaction of Copper and Nitric Acid in presence of Metallic Nitrates.*" (Part II.). By Edward Henry Rennie and William Ternent Cooke.

The authors find that whereas in previous experiments at 59° and with 2N-acid, potassium nitrate had apparently no effect, and rubidium and cæsium nitrates a retarding effect on the dissolution of copper in dilute nitric acid, all these nitrates have either an accelerating or retarding effect according to the conditions of temperature and concentration. With the same concentration of acid, and with potassium nitrate, the lower the temperature the less is the acceleration (it often becomes retardation), whereas the higher the temperature, the greater is the acceleration. With the same temperature, increase of concentration of acid tends to lessen acceleration. These statements seem also to hold good with rubidium and cæsium nitrates. The authors also find that the effect of the increase of volume of acid due to the solution in it of considerable quantities of nitrates is a factor not to be overlooked, inasmuch as it obviously diminishes the concentration of the acid, and of nitrous acid or other products formed during the reaction. They conclude that these fresh results tend to confirm the opinions expressed by them in their previous paper (*Trans.*, 1908, xciii., 1162).

45. "*The Mechanism of Doebner and von Miller's Quinaldine Synthesis.*" By Humphrey Owen Jones and Percy Edwin Evans.

Doebner and von Miller's well-known synthesis of quinoline derivatives from an aldehyde and an aromatic amine by heating with hydrochloric acid is represented by the equation $C_6H_5{\cdot}NH_2 + 2CH_3{\cdot}CHO = C_{10}H_9N + 2H_2O + H_2$ in the simplest case.

The molecule of hydrogen is used up mainly in reducing some of the aldehyde.

During the examination of the aldol bases, $R{\cdot}NH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$, formed from *m* 4-xylidine and similar amines (Jones and White, *Trans.*, 1910, xcvii., 632), the transformation of these into quinoline derivatives by heat or by acids in the cold was studied, and was found to take place without perceptible evolution of gas.

The aldol bases cannot be reduced by nascent hydrogen, and the change was therefore further examined. It was found that no gas was evolved, and that the transformation of the aldol base from *m*-4-xylidine at 140—250° is represented by the following equation :—

$$2C_6H_3Me_2{\cdot}NH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO = C_9H_4Me_3N + C_9H_8Me_3N + 2H_2O.$$

The change is practically quantitative, equimolecular quantities of 2 : 6 : 8-trimethylquinoline (m. p. 45 – 46°) and 2 : 6 : 8-trimethyltetrahydroquinoline (m. p. 50—51°, b. p. 260—261°) being produced.

Similar results have been obtained with *p*-toluidine. The synthesis of these quinoline and tetrahydroquinoline derivatives can be effected in this way, namely, by isolating the intermediate aldol base and heating it, much more cleanly and economically than by the usual method.

46. "*A Synthesis of Derivatives of Phenothioxin.*" By Thomas Percy Hilditch and Samuel Smiles.

The ethers of *p*-cresol and *p*-chlorophenol sulphoxides show the normal reactions of the thionyl group in sulphuric acid solution, whilst the corresponding hydroxy-sulphoxides do not. This abnormal behaviour is due to the formation of the cyclic phenothioxin derivatives, for example, $CH_3{\cdot}C_6H_3{<}^{\text{-O-}}_{\text{SO}}{>}C_6H_3{\cdot}CH_3$, which have been isolated. The general character of the phenothioxin group was discussed.

47. "*The Nitration of Acetylbenzoin and of Stilbenediol Diacetates.*" By Arthur Gordon Francis and Charles Alexander Keane.

Acetylbenzoin, on nitration with fuming nitric acid at 0°, yields a *mononitro*-compound which is also obtained when the nitration is carried out at −15° in acetic anhydride solution by means of nitre and sulphuric acid. It forms almost colourless leaflets, melting at 125° (uncorr.). It is sparingly soluble in ether or light petroleum, readily so in chloroform, acetone, or benzene, and somewhat less soluble in boiling 90 per cent alcohol. When oxidised with sulphuric acid and potassium dichromate, it yields molecular proportions of acetic acid, benzoic acid, and *p*-nitrobenzoic acid. It has thus the following structure :—

$$\underset{(1)}{NO_2{\cdot}C_6H_4}{\cdot}\underset{(4)}{CH(OAc){\cdot}CO{\cdot}C_6H_5}.$$

Hydrolysis with acids or alkalis yields, not nitrobenzoin,

but condensation compounds, which are under further investigation.

Both α-stilbenediol diacetate (melting-point 153°) and β-stilbenediol diacetate (melting-point 110°), on nitration at −15° in acetic anhydride solution with nitre and sulphuric acid yield benzoin mononitrate and a small quantity of a substance, possibly nitrobenzoin, melting at 188°, whilst β-stilbenediol diacetate is at the same time partly converted into the α-compound. No benzoin nitrate is formed at 0° or at −25°.

Benzoin mononitrate, $C_6H_5{\cdot}CH(O{\cdot}NO_2){\cdot}CO{\cdot}C_6H_5$, crystallises from 90 per cent alcohol in brilliant white plates, melting at 167° (uncorr.). It is very sparingly soluble in ether or light petroleum. On hydrolysis with potassium hydroxide, it yields benzoin and potassium nitrate, and on heating with concentrated nitric acid benzil is formed.

48. "*Experiments on the Formation of 4(or 5)-β-Aminoethylglyoxaline from Histidine.*" By Arthur James Ewins and Frank Lee Pyman.

It has been found that by heating histidine (monohydrochloride) with (*a*) concentrated hydrochloric acid, (*b*) dilute (20 per cent) sulphuric acid, and (*c*) potassium hydrogen sulphate in closed vessels at 265—270°, a maximum yield of 20 to 25 per cent of the theoretical amount of the base, 4(or 5)-β-aminoethylglyoxaline (formed from histidine by removal of carbon dioxide), can be obtained. At temperatures below 240° no formation of the base takes place, whilst at 240—250° the main product of the reaction is racemic histidine.

By directly heating histidine above its melting-point, only very small amounts of the base are produced. Somewhat better results were obtained by fusing the monobenzoyl derivative of histidine at about 240° in a vacuum and subsequently hydrolysing the reaction product.

Some new salts of racemic histidine, or 4(or 5)-β-aminoethylglyoxaline, and the dipicrate of natural histidine were described.

49. "*The Dissociation of Cupric Bromide and some Forms of Glass Manometer.*" By Colin Gyrth Jackson.

Three varieties of glass manometer were described, whereby it is possible to measure pressures of vapours in contact with no other material. Values of the dissociation pressure of cupric bromide at a series of temperatures were given and their connection shown to be adequately represented by an equation involving the constancy of the heat of dissociation, the applicability of the simple gas laws to bromine under the conditions of the experiment, and the first and second laws of thermodynamics.

50. "*The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method.*" By James Riddick Partington.

An account was given of experiments on three hydrates, in which the dissociation pressures have been measured by a dynamical method. The results were shown to be in agreement with the view referred to in a previous communication (*Proc. Chem. Soc.*, xxvii., 12).

51. "*The Influence of Conjugated Linkings on General Absorptive Power.* Part I. *The Absorption Spectra of some Benzene Derivatives.*" By Cecil Reginald Crymble, Alfred Walter Stewart, Robert Wright, and William Gerald Glendinning.

An examination of the absorption spectra of twenty-eight benzene derivatives (supported by a similar investigation of about the same number of aliphatic and alicyclic substances) has shown that it is possible to trace some connection between the chemical structure of an unsaturated carbon compound and its general absorptive power. Of two isomeric substances containing two or more double bonds, the compound the molecule of which contains the longest chain of conjugated linkings appears to have the greater power of general absorption in the region of the spectrum above that in which any absorption band makes its appearance. In the case of two isomeric substances like atropic and cinnamic acid, the isomeride, which contains what Thiele terms "crossed double bonds" (for example, atropic acid), will have less absorptive power than the isomeride which contains a simple conjugated system of linkings, such as occurs in cinnamic acid. It was pointed out that this rule will furnish additional assistance in the determination of the constitutions of terpenes containing two double bonds the relative positions of which are difficult to ascertain.

52. "*The Optical Properties of Acids containing Three Hydrocarbon Residues directly Attached to an Asymmetric Carbon Atom.* Part I. *The Synthesis of β-Phenyl-β-methylvaleric Acid and of* as-*Methylethylsuccinic Acid.*" By John Kenneth Harold Inglis.

Compounds containing an asymmetric carbon atom might be expected to be very stable when subjected to the action of racemising agents. In order to investigate this question, *β-phenyl-β-methylvaleric acid*, $CMePnEt{\cdot}CH_2{\cdot}CO_2H$, has been prepared, but as the substance is a liquid, and its salts are difficult to crystallise, it is not a suitable substance for this purpose. *as*-Methylethylsuccinic acid, however, is crystalline, and can be obtained fairly easily by the method used by Higson and Thorpe (*Trans.*, 1906, lxxxix., 1467). Methyl ethyl ketonecyanohydrin condenses with the sodium derivative of cyanoacetic ester to give a liquid boiling at 165°/19·5 mm., which has the formula $C_{10}H_{14}O_2N_2$. This liquid gives *as*-methylethylsuccinic acid on hydrolysis. The acid has been resolved by crystallisation of its quinine salt.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, February 20th, 1911.

Mr. E. Grant Hooper in the Chair.

The following papers were read and discussed:—

"*The Composition of the Acids flowing from the Thomson Displacement Apparatus for the Manufacture of Gun-cotton.*" By G. W. MacDonald.

The cotton waste is immersed in the nitrating acid in shallow earthenware pans provided with a stop-cock at the lowest point. When nitration is complete this cock is opened, and, as the acid slowly runs away, the water runs in on top at an equivalent rate, and the acid is thus completely displaced from the gun-cotton. The course of the displacement has been followed by analysing samples of acid which were drawn, at fairly frequent intervals, as displacement proceeded. The results show that sulphuric acid is displaced at a relatively much more rapid rate than nitric acid. The percentage of the latter remains very constant for a considerable period of the displacement, and during a short time actually rises. The suggestion is made that this may probably be due to a selective adsorption of nitric acid by the gun-cotton fibre, or that a labile nitrate has gradually broken up, as the water content of the acid flowing away gradually increases. The rise of temperature is very regular—about 1° C. for every fifteen minutes during the first 150 minutes of displacement. The loss to the drains amounts to 0·4 per cent of the acid originally used, or only 0·08 lb. total loss of both acids per lb. of gun-cotton produced.

(I.) "*Ammonium Sulphate and its Instability*, and (II.) *the Hydrolysis of Ammonium Salts.*" By Watson Smith.

The author shows by references and quotations, &c., that errors and omissions as to the true properties of ammonium sulphate, as well as other ammonium salts, are being continually perpetuated in our highest class textbooks and works of reference, and he proceeds to demonstrate how far reaching and insidious is the mischief wrought thereby, both as regards analytical chemistry and technology.

Thus, a melting-point of 140° C. is attributed to ammonium sulphate which has no melting-point. This salt

is said only to commence decomposition above 280° C., when in truth it commences at temperatures below 100° C. to lose ammonia. It is said to begin subliming at 280° C., though not without decomposition, whereas it is incapable of subliming. Very few indeed of the larger works pay any attention to the behaviour on heating of ammonium sulphate solutions and the behaviour of other ammonium salt solutions. Thus those extremely few works that are correct appear in the questionable position of making contradictory statements as regards the classical or standard works.

It is pointed out that the statements attributed ro Marchand in Gmelin's earliest work, and almost totally wrong, have been perpetuated up to date, and are in part recorded in the *Chemiker Kalendar* for 1911, *i.e.*, over a period of eighty years. The investigations of Pebal, Debbits, Gernez, Albert Leeds, Fittig, W. Smith, Reik, and Naumaun and Rucker are pointed to, and briefly the results stated.

Especially the results of hydrolytic dissociation of ammonium salts in aqueous solution are described, and the effect of ignorance of the law governing these is incidentally demonstrated from our own *Journal* as recently as 1909, as well as in certain analytical methods (such as those of Rose and Wohler) and also in some technical processes. The author gives some hydrolysis results with ammonium salts not yet recorded, i.e., with ammonium phthalate, arseniate, and borate, together with a singular fact in connection with the hydrolysis of ammonium chloride.

"*A Study of some Reactions in Gels.*" By E. Hatschek.

This paper describes the results of a series of experiments in which insoluble calcium, barium, lead, and silver compounds were precipitated in gelatin and agar gels, special attention being devoted to the size and form of the particles produced. The reactions took place in gelatin and agar gels, containing a small percentage of a soluble calcium, barium, lead, or silver salt, which were covered by solutions of salts capable of forming insoluble compounds with those dissolved in the gel. It was found in all these experiments that the precipitates formed crystals or more generally crystalline aggregates exceeding in size very considerably those obtained from aqueous solutions of the same concentrations, and that there was a marked tendency towards the formation of spherical aggregates, and in many instances perfect spherolites. Macroscopic masses, *e.g.*, nodules of calcium sulphate up to 3 mm. diameter, were obtained in several cases. Photo-micrographs of various preparations of calcium sulphate, calcium carbonate, barium carbonate, barium oxalate, barium silicofluoride, lead sulphate, lead chloride, lead bichromate, and lead ferrocyanide were shown; also some of the actual gels containing lead iodide, barium carbonate, silver bichromate, as well as some of the insoluble compounds recovered from the gels. The experiments threw some light on the formation of large masses of insoluble compounds in organisms in which reactions practically always take place in colloidal media; possibly also on the formation of large crystals or aggregates of minerals which are highly insoluble and yet not likely to be of igneous origin.

"*A New Still-water Gas Calorimeter.*" By J. H. Coste and B. R. James.

The authors describe a calorimeter designed by Mr. Coste for the determination of the gross calorific power of gas by the combustion of one-twentieth cubic foot. The apparatus consists of two parts, (*a*) the gas-holder and (*b*) the calorimeter.

(*a*) The gas-holder is constructed on Mariotte's principle to deliver gas at a constant rate and pressure throughout the whole period of an experiment. A simple by-pass is inverted in the inlet tube, through which water enters the holder, so that the rate of flow can be greatly reduced as the water level approaches a metal point, centrally placed in the holder, which defines the volume of gas to be burnt. The contact is very well defined, and the volume is independent of any small error of levelling of the apparatus. The burner, which is of porcelain, is swung under the calorimeter as the contact is made. The transfer is very rapid and the errors are small.

(*b*) The calorimeter vessel, of nickel-plated copper, holds about 2·3 kilos. of water, and is itself placed within a large annular vessel (from which it is separated by an air space) holding about 7—8 litres of water; this greatly decreases the influence of surroundings. The volume of water in the calorimeter is defined by contact of its surface with a metal point depending from a wooden bridge which carries the thermometer and the bearing for a double horse-shoe stirrer of very efficient pattern. The gas is burnt within the calorimeter in a central combustion chamber of corrugated copper tubing. The products of combustion pass into an oval copper box, against the sides of which they are forced, and down side tubes of flattened corrugated copper tubing. The cooling of the products is very complete.

The rise of temperature for gas of 140 calories gross is about 3° C. The following errors have been investigated. Those due to (*a*) variation in amount of gas burnt; (*b*) I. Adjustment of the amount of water in the calorimeter. II. Imperfect mixing of the water. III. The water equivalent. IV. Radiation, evaporation, conduction, and friction of the stirrer. V. Imperfect cooling of the escaping gases. VI. Water vapour in the escaping gases. Their magnitude is small and the method of correction simple.

The calorimeter was made by William Sugg and Co., Ltd.

INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 1st, 1911.

Dr. George Beilby, F.R.S., President, in the Chair.

The annual accounts were received on the motion of Mr. E. Grant Hooper, seconded by Mr. A. E. Ekins, and a vote of thanks was accorded the Honorary Auditors.

Mr. David Howard, in moving the reception of the Report of the Council, after referring to the work of the past year, remarked on the influence of the Institute in providing qualified chemists for industries, whereby leading manufacturers were led to appreciate more and more the practical value of science.

Dr. John A. Voelcker, in seconding, referred especially to the work of the Honorary Corresponding Secretaries in various parts of the Empire who assisted in the conduct of local examinations, and were helpful to Fellows of the Institute taking appointments abroad, while they constituted a bond of union with chemists at home, keeping the Council informed as to the progress and prospects of professional chemists in their respective districts.

The Report was duly received, and the meeting proceeded to select Honorary Auditors for the ensuing year, Mr. R. E. Alison, Dr. L. T. Thorne, and Mr. L. Myddelton Nash being appointed.

The President then delivered his Address. After referring to the losses of the Institute by death, mentioning especially Prof. Campbell Brown, Mr. Michael Carteighe, and Mr. Oscar Guttmann, he dealt with the progress and work of the Institute. The Membership continued steadily to increase, notwithstanding the high standard of the Examinations; while the position of the Institute as an organisation existing for public service never stood so high as at the present time. Over 96 per cent of the appointments of Public Analysts in the United Kingdom are held by Fellows of the Institute, the Final Examination in the Chemistry of Food and Drugs being conducted on lines prescribed by the Local Government Boards and especially recognised by them for these appointments.

The Council had under consideration the institution of a series of lectures, the object of which would be to bridge over the gap between academic training and practice. Without depreciating the value of a broad scientific

education, it was realised that students entirely trained in an academic atmosphere missed some of the advantages of the old system of private pupilage in the laboratories of practising Fellows or in works. This loss was met in some instances by students preparing for the Final Examination in such laboratories; but there was a need for a means of introducing something analogous to the clinical instruction afforded to medical students. It was proposed, therefore, to ask Fellows having expert knowledge to give lectures which would give students an insight into the actual work of the chemist, whether engaged in the application of his science to commerce and industry or to the scientific control of the affairs of daily life. Apart from the value of the information which could be imparted by such experts, considerable advantage would accrue to the students from the mental contact with such men, while they would acquire a proper sense of proportion in respect of the work of chemists in various branches of practice.

The President then remarked on the successful working of the Appointments Register, by which means the Institute introduced properly qualified chemists to authorities and manufacturers requiring their services, and he acknowledged the valuable help given by the Honorary Corresponding Secretaries of the Institute to members taking up appointments in various parts of the Empire.

Continuing, he referred to the appeal which had been made for funds for new buildings. It has been estimated that £15,000 would be required for this purpose, and the Council were able to record promises amounting to £7566, of which about £5000 had actually been received. This included contributions from four of the great City Companies and from a few manufacturing firms. He hoped that others would show their appreciation of the work of the Institute in the same practical manner, and he appealed to the Fellows and Associates themselves, as far as they were able, to promote the successful raising of the fund.

Prof. MELDOLA, in moving a hearty vote of thanks to the President for his Address, said it would give him much pleasure to see the Institute take an active part in the education of chemists, and he cordially supported the new departure as to the institution of the proposed lectures, which would make the student realise more fully the value of the practical side of his subject. The Institute had always been happy in the selection of its officers, and he (Prof. Meldola) paid a high tribute to the services of Dr. Beilby, the present President, for his zeal and attention to the affairs of the Institute.

Mr. A. CHASTON CHAPMAN, having seconded, the vote was carried by acclamation.

The following Fellows were re-elected as Censors:—Prof. Percy F. Frankland, Mr. David Howard, Prof. J. Millar Thomson, and Sir William Tilden.

On the motion of Mr. WALTER F. REID, and seconded by Mr. JOHN HUGHES, a vote of thanks was accorded to the retiring Officers and Members of Council for their services.

Mr. BLOUNT, a retiring Examiner, and Mr. GRANT HOOPER, a retiring Vice-President, having responded, the preceedings terminated.

The following were elected Officers and Council.

President—George Thomas Beilby, LL.D., F.R.S.

Vice-Presidents—Frank Clowes, D.Sc.; Percy Faraday Frankland, LL.D., Ph.D., F.R.S.; George McGowan, Ph.D.; Raphael Meldola, F.R.S.; John Millar Thomson, LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., F.R.S.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Francis William Frederick Arnaud; Edward John Bevan; Bertram Blount; William John Atkinson Butterfield, M.A.; Francis Howard Carr; Charles Edward Cassal, Col., V.D.; Alfred Chaston Chapman; Arthur Crozier Claudet, A.R.S.M.; James Connah, B.Sc.; William Salvador Curphey; Cyril Dickinson, B.Sc.; James Johnston Dobbie, Ph.D., LL.D., F.R.S.; William Porter Dreaper; John Alfred Foster; Walter Charles Hancock, B.A.; Frank William Harbord, A.R.S.M.; Frederick Gowland Hopkins, M.A., M.B., D.Sc., F.R.S.; William Jackson Pope, M.A., M.Sc., F.R.S.; Thomas Slater Price, D.Sc.; Ph.D.; Charles Proctor; Sir Boverton Redwood, D.Sc.; Henry Droop Richmond; Alfred Smetham; Edward William Voelcker, A.R.S.M.; John White; Sydney Young, D.Sc., F.R.S.; William Maurice Gathorne Young.

NOTICES OF BOOKS.

An Introduction to Physical Chemistry. By JAMES WALKER, LL.D., F.R.S. Sixth Edition. London: Macmillan and Co., Ltd. 1910.

IN revising this book in preparation for the issue of the sixth edition the results of the latest work in physical chemistry have been incorporated in it, and where further investigation has brought errors to light in earlier conceptions the necessary corrections have been made. New chapters on subjects which have shown important developments in the last few years have been added. Thus an outline is given of methods of investigating alloys; typical temperature—composition diagrams, of which so much use has been made recently, are reproduced and carefully explained, and the conclusions to be drawn from the study of them are summarised. Chapters have also been added on Hydrates, Colloidal Solutions, and Radio-active Transformations respectively, in which the latest advances are adequately discussed, and with these additions the book will maintain its position as one of the best, and, for its size, most comprehensive elementary treatises on physical chemistry extant.

Introduction to Practical Organic Chemistry. By A. M. KELLAS, B.Sc. (Lond.), Ph.D. (Heidelberg). London: Henry Frowde; Hodder and Stoughton. 1910.

THE course of practical chemistry described in this book covers the syllabus of the Preliminary Scientific Examination of London University and Stages I. and II. of the Board of Education syllabus, as well as the work prescribed by Oxford and Cambridge and the Welsh Universities. The directions are clear and systematically presented, and an excellent feature is the stress laid upon general methods and reactions, to which the student's attention is constantly called. The detection of the elements in organic compounds is first discussed, and the common laboratory operations of organic chemistry are described in sufficient detail for the student who has had some practice in manipulation. These operations are classified as those employed in methods of preparation, including filtration, crystallisation, salting out, &c., and those employed in the determination of physical constants. Then the preparation of a large number of typical and important compounds is described, and schemes for the identification of the substances included in the syllabus of the Board of Education (Stages 1 and 2) are given. A convenient summary is included of methods of detecting the most important organic groups in a compound, and some quantitative analysis is described. The book is a thoroughly good example of a laboratory text-book, and merits extensive use in the junior classes of the Universities and in Technical Schools.

Introduction to General Chemistry. By JOHN TAPPAN STODDARD, Ph.D. New York: The Macmillan Company. 1910.

ALTHOUGH the author of this book recognises that the chief value of a course of chemistry is the training in a

scientific habit of thought which a well-planned scheme should give, and that the knowledge of the facts gained is of very secondary importance, he has put too much material before the student for a first year's work. Nevertheless, on the whole, the book will call the reasoning power rather than the memory into play. In the earlier chapters perhaps an undue amount of theory is introduced, but the treatment is decidedly suggestive and interesting. The title to the book is not happily chosen, for it is hardly applicable to what is really an elementary text-book of inorganic chemistry.

Chemistry of Coal. By Myles Brown, M.E. Wigan: Published at the Office of "The Science and Art of Mining."

The study of this book may possibly help the purchaser and consumer of coal to get a more complete and better grounded knowledge of the value and uses of different classes of coal, and may thus enable him to practise economy in its consumption. The special characteristics of all the more important kinds of coal are discussed, and methods of analysis are given in outline, the conclusions to be drawn from the results obtained being shortly explained; methods of determining calorific power are treated fairly fully. Considering the class of readers for whom the book seems mainly intended, there appears to be a good deal of purely scientific information in it which is of very little value; for example, it is useless for the practical man to know that sulphur is a hexad element. Moreover, the information is not always correct, for the formula of potassium chlorate is twice given as $KClcO_3$, and it is stated that potassium nitrate on heating loses half its weight of oxygen.

Some Effects of a Harmful Organic Soil Constituent. By Oswald Schreiner and J. J. Skinner. Washington: Government Printing Office. 1910.

This bulletin contains an account of a study of the effects on the growth of wheat of harmful organic compounds in the soil; the methods of investigation employed are fully described, illustrations of different cultures are reproduced, and the detailed results of analyses are given in tabular form. The authors have definitely proved that dihydroxystearic acid hinders the growth of wheat plants. They have determined the exact conditions in which it is most harmful, and are able to describe the effects of the compound upon the plants; they have observed that in the presence of mainly nitrogenous fertilisers the acid is relatively much less harmful. Incidentally the investigation has thrown some light upon the relation between plant growth and the action of fertilisers.

Zinc, Cadmium, Cuivre, Mercure. ("Zinc, Cadmium, Copper, Mercury"). By A. Bouchonnet. Paris: Octave Doin et Fils. 1911.

This volume belongs to the Bibliothèque de Chimie, which when completed is to consist of thirty-one monographs on general, inorganic, and organic chemistry, written by various authors, each of whom has a special knowledge of the subject entrusted to him. The editor intends that the volumes shall be interesting and readable, and shall contain the essentials of the subject without going into minute details, and this volume appears to answer to these general requirements. It gives a succinct account of the descriptive chemistry of the four metals, discussing the occurrence, preparation, and properties of the elements themselves and their chief compounds. Technical questions are not discussed, nor is the physical chemistry of the metals treated, but, from a descriptive point of view, the book appears to be sufficiently full for the purposes of the scientific man who is not an expert.

The M.C.C. Chart of the Elements. London: The Metallic Compositions Co.

This chart of the elements gives a complete list of all the known elements arranged according to the Periodic System. The chart measures 34" by 40", and thus there is room on it to give details of the most important properties of each element. In the still unfilled spaces general information is given relating chiefly to the metals. In conjunction with the chart a booklet is issued explaining the use of the Periodic Table and the meaning of the terms employed, and including some discussion of its relation to speculative thought. The chart is also issued in roller form to hang upon the wall of the laboratory, and specimens of the elements can be procured from the publishing firm to illustrate the table. The information given in the chart appears to be accurate and well chosen, and it will serve to impress upon the student the relationship between the elements of the same family and the connection between position in the table and chemical and physical properties.

OBITUARY.

PROFESSOR VAN 'T HOFF.

We much regret to have to announce the death of Prof. J. H. van 't Hoff, which recently took place at Steglitz, after a somewhat protracted illness.

Jacobus Henricus van 't Hoff was born at Rotterdam on August 8th, 1852. He was educated at Delft, Leyden, Bonn, and Paris, and, stimulated by the inspiring lectures of Kekulé and afterwards of Wurtz, he early displayed remarkable powers, his singularly original mind being revealed in the theoretical papers he published while still quite a young man. His bold speculations are well exemplified in the hypothesis of optical isomerism, which he and Le Bel independently put forward in 1874, and in virtue of which he must be regarded as one of the founders of the theory of stereoisomerism. In 1876 he was appointed a lecturer in the Veterinary College at Utrecht, having previously (1874) published his first important treatise "La Chimie dans l'Espace." He became Professor of Chemistry at the University of Amsterdam in 1878, and during the next eighteen years he continued to show considerable activity in contributing articles and papers to the scientific journals, in which he worked out his theory of the arrangements in space of the atoms in carbon compounds, a theory which, after meeting with strenuous opposition from many well-known chemists of the day, finally came to be accepted as providing an adequate explanation of the observed facts. Other important works published during this period were "Dix Années dans l'Histoire d'une Théorie" (1887); "Ansichten über die Organische Chemie" (1878—1881); "Etudes de Dynamique Chimique" (1884); and "Lois de l'Equilibre Chimique" (1885). In 1887, together with Prof. Ostwald, he founded *Zeitschrift für Physikalische Chemie*, which he continued to edit until his death. He became a Professor at the University of Berlin, and a member of the Berlin Academy in 1896. Of late years his researches have chiefly lain in the domain of physical chemistry, and include the application of the principles of thermodynamics to chemical problems, the investigation of the laws of osmotic pressure and of the laws of solutions. The results of his researches on the chemical equilibrium of salts in solution are of great importance from a geological point of view, as explaining the origin of the Stassfurt and other saline deposits.

Professor van 't Hoff was universally regarded by the chemists of all nations as one of the most illustrious masters of the science, and his labours were rewarded by many distinctions and orders, among them the Nobel Prize, which he received in 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 1, January 3, 1911.

This number contains no chemical matter.

No. 2, January 9, 1911.

Probable Chemical Properties of Radium and its Compounds.—M. de Forcrand.—In the list of the metals of the alkalis and alkaline earths when arranged in order of the heats of formation of their haloid salts and their oxides, radium undoubtedly comes between barium and sodium. From this fact it may be calculated that the heat of formation of its chloride is practically zero, and its solubility is nearly independent of the temperature. The following table gives the solubility of the salts at 15° :—

	Parts per 100 of water.
Chloride	35 to 36
Bromide	about 100
Iodide	about 180
Fluoride	1 to 2
Oxide	10 to 20

A strong base, $Ra(OH)_2$, should be formed by the union of the oxide with water; this base would be rather more stable than $Ba(OH)_2$, but would dissociate more easily than NaOH. A fairly stable dioxide RaO_2 should exist, and a carbonate which would hardly decompose at a red-heat. A hydride, RaH_2, decomposing at about 900°, should be formed. The action of calcium or lithium on the fluoride ought to give the metal.

Electrical Properties of Aluminium-Magnesium Alloys.—Witold Broniewski.—If curves are drawn in which the abscissæ are the percentage by volume of the constituent metals and the ordinates the electrical properties of the corresponding alloys of aluminium and magnesium, it appears that probably two definite compounds, AlMg and Al_2Mg_3, exist, but the curves do not confirm the existence of compounds Al_4Mg and $AlMg_2$.

General Method of Preparing Anhydrous Chlorides.—Ed. Chauvenet.—Carbon oxychloride very readily transforms metallic oxides into anhydrous chlorides according to the equation $MO+COCl_2=CO_2+MCl_2$. The yields obtained are very satisfactory, especially in the case of the chlorides of the rare earths, titanium, zirconium, chromium, nickel, &c.

Ketones Derived from Toluic Acids. — J. B. Senderens.—With the toluic acids catalysis in presence of thoria leads to the formation of the mixed aromatic ketone and the symmetrical fatty ketone according to the equation—

$$C_6H_4(CH_3)CO.OH+3RCO.OH = C_6H_4(CH_3)CO.R+RCOR+2CO_2+2H_2O.$$

The two ketones can readily be separated by distillation. The symmetrical aromatic ketone is not formed. The author has prepared the following ketones by this method —cresylmethyl ketones, cresylethyl ketones, cresylpropyl ketones, cresylisopropyl ketones, cresylisobutyl ketones. They are all colourless liquids, with agreeable odours. Their semicarbazones are easily prepared in the crystalline state.

New Thiophenic Compound $C_{10}H_6S_2$ and its Derivatives.—M. Lanfry.—When vapours of sulphur and naphthalene are passed through a red-hot iron tube a tarry mass collects at the end of the tube; by extraction with alcohol two crystallising products can be obtained. The first crystallises in red prisms, and from its reactions is evidently either phenothiophene or its symmetrical isomer phenodithiophene. Its acetic solution is very readily oxidised with hydrogen peroxide, yielding first a compound of formula $C_{10}H_6S_2O_2$, and then $C_{10}H_6SO_4$. The first of these behaves like a paradiphenol.

Condensation of Acetic Ether with its Higher Homologues.—A. Wahl.—It is possible to induce the condensation of acetic ether with its homologues by means of sodium, butyric ether being thus converted into butyryl acetate with a yield of 18 to 20 per cent. Nitrous vapours act on ethyl butyryl acetate, transforming it into the α3-diketone.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Major C. Ashburnham, Mrs. Roy-Batty, Colonel E. H. Bethell, D.S.O., Mr. L. M. E. Dent, Mr. M. de Selincourt, Mr. J. J. Dobbie, Miss Greaves, Mr. D. C. J. H. Kropveld, Miss S. McNaughton, Mr. F. W. Mander, Dr. Ettie Sayer, Mr. C. J. Tabor, Dr. W. Wahl, and Mrs. Watson were elected Members. Prof. H. E. Armstrong, F.R.S., has been nominated the Delegate of the Royal Institution at the celebration of the Centenary of the Royal Frederick University of Christiana, and Sir James Crichton-Browne, M.D., F.R.S., as Delegate at the celebration of the 500th Anniversary of the University of St. Andrews. The Secretary reported the decease of Prof. J. W. Bruhl, an Honorary Member of the Institution, and a resolution of condolence with the family was passed.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Royal Society of Arts, 8. "Applications of Electric Heating," by Prof. J. A. Fleming, F.R.S.

TUESDAY, 14th.—Royal Institution, 3. "Crystalline Structure—Mineral, Chemical, and Liquid," by A. E. H. Tutton.

—— Faraday Society, 8. "Some Properties of Aluminium Anode-films," by G. E. Bairsto and R. Mercer. "Weight of a 'Normal' Litre of Hydrogen Chloride and the Atomic Weight of Chlorine," by F. P. Burt and R. W. Whytlaw-Gray. "A Physico-chemical Study of Mercury-sodium Alloys or Sodium Amalgams," by E. Vanstone. "Surface Effects between Mercury and certain Solutions, and an Electro-chemical Method of Estimating Dissolved Oxygen," by S. W. J. Smith and W. F. Higgins.

WEDNESDAY, 15th.—Royal Society of Arts, 4.30. "The Adulteration of Food," by Col. C. E. Cassal.

—— Microscopical, 8. "Morphology of the Organisms concerned in the Production of Acute Intestinal Toxæmia in Infants," by Dr. R. Vincent. "Anomalies in Objective Screw Threads," by F. W. W. Baker. "Some New Objectives and Eye-pieces by R. Winkel, of Gottingen," "An Objective Mount with an Iris," and "The Variable Microscope," by E. M. Nelson. "Apparatus for Microphotography with Microscope standing in any Position, especially in inclined Position," by Sr. Domingo Orueta.

THURSDAY, 16th.—Royal Institution, 3. "Giants and Pygmies," by Prof. Arthur Keith, M.D.

—— Royal Society of Arts, 4.30. "Education in India," by Claude H. A. Hill, I.C.S.

—— Royal Society. "Gametogenesis of the Gallfly, *Neuroterus lenticularis*," by L. Doncaster. "Action of the Venom of *Echis carinatus*," by Sir T. R. Fraser and Dr. J. A. Gunn. "Further Researches on the Development of *Trypanosoma gambiense* in *Glossina palpalis*," by Col. Sir D. Bruce and others. "Spontaneous Cancer in Mice," by Dr. M. Haaland.

—— Chemical, 8.30. "Apparatus for the Maintenance of Constant Pressures above and below the Atmospheric Pressure—Application to Fractional Distillation," by J. Wade. "Interaction of Aromatic Disulphides with Sulphuric Acid," by W. G. Prescott and S. Smiles.

FRIDAY 17th.—Royal Institution, 9. "Water Supply," by John H. Balfour-Browne, K.C.

SATURDAY, 18th.—Royal Institution, 3. "Radiant Energy and Matter," by Prof. Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. CIII., No. 2677.

STUDIES OF THE PROCESSES OPERATIVE IN SOLUTIONS.

XVIII.—The Depression of Electrical Conductivity by Non-Electrolytes.

By HENRY E. ARMSTRONG and DAVID CROTHERS.

The observations recorded in communication No. XII. of this series by F. P. Worley, taken in conjunction with all previous work on the subject, serve apparently to establish the paradox that the rate at which cane sugar is hydrolysed by acids is dependent only in a very minor degree on the concentration of the sugar; even still more remarkable is the fact established by R. J. Caldwell (Part I.) that large amounts of glucose and other similar sugars may be added to the solution without altering appreciably the rate at which the cane sugar is resolved, although salts generally have a large "concentrating" influence and the monohydric alcohols of the ethylic series a not inconsiderable depressant effect (compare XIII). From these considerations alone it may be concluded that the inactivity of sugars generally in altering the rate of change is apparent only and that counteracting influences are at work in the solution tending to reduce the activity of the acid; the argument is equally applicable to the hydrolyte—to cane sugar, as it is to be supposed that hydrolyst and hydrolyte are affected reciprocally.

Previous observations by Caldwell, by ourselves, by Caldwell and Whymper and by Glover have shown that the electrical conductivity of solutions of salts is much reduced by glucose and other sugars—far more than by any other non-electrolyte. This circumstance is clear proof that great disturbances are produced by the presence of such non-electrolytes; it cannot well be argued that these are the consequence of changes merely in the viscosities of the solutions, as such changes presumably are themselves but evidence of alterations in the conditions affecting both solvent and solute. If the effect on hydrolytic change be not obvious, therefore, it is to be supposed that the alteration is in some way masked by changes which counteract the depressant influence which it is to be supposed all "neutral" substances would exercise, whether it be assumed that they act only mechanically by interference or that they also condition changes in the composition of the medium.

To obtain further evidence as to the nature of the influence exercised by non-electrolytes, we have considerably extended our observations on the effect of non-electrolytes on the conductivity of aqueous solutions of electrolytes.

The conductivity was first determined of a solution containing a single gram-molecular proportion of the electrolyte in 1000 grams of water; a similar solution containing in addition either a single or half a molecular proportion of the non-electrolyte was then prepared and the conductivity of the mixture determined. The results are embodied in the accompanying table.

The striking fact brought out in this table is the great influence exercised by methylic alcohol and its homologues and the remarkable manner in which this influence increases as molecular weight increases *and the solubility of the alcohol diminishes*. Glycol and glycerol are less active depressants than the corresponding monohydric alcohols; acetaldehyde and acetone, which are both present in solution to some extent as "diols," apparently differ but little from glycol. The high molecular activity of ether and paraldehyde (presumably little short of twice that given as the effect of one-half of a molecular proportion) is very striking.

The effect produced by the sugars is also very great; it may be noted that the increase in "molecular" effect as the complexity increases, in the case of the three compounds cited, is not far from proportional to the increase in the number of the oxygen atoms.

The explanation we desire to advocate is that compounds such as the higher monohydric alcohols we have studied, ether and paraldehyde are but loosely and to a minor extent associated with the "water" in their aqueous solu-

Effect of various Non-electrolytes in Reducing Molecular Electrical Conductivity of Electrolytes. Weight-normal Solutions.

Electrolyte	NaOH		LiCl		NaCl		NH_4Cl		KCl		KBr		KI	
Temperature at which observation was made ..	0°	25°	0°	26°	0°	25°	0°	25°	0°	25°	0°	25°	0°	25°
Molecular conductivity of the electrolyte	103·1	180·0	40·3	74·3	47·6	86·3	65·0	112·2	65·3	112·2	68·5	116·3	70·2	118·7
Proportion of added substance.	Percentage reduction of conductivity.													
1 gram-mol. methanol ..	—		9·3	7·3	—		8·8	6·7	9·0	6·7	9·0	6·7	8·7	6·5
1 „ ethanol ..	18·5	14·5	18·0	13·1	—		16·3	12·2	16·2	12·4	15·9	12·0	15·6	11·5
1 „ propanol ..	23·7	19 0	24·1	17·5	—		—		21·7	16·5	22·0	16·2	—	
½ „ „ ..	—		—		—		—		12·0	8·9	—		—	
½ „ *iso*butanol .	—		—		—		—		14·4	10·6	—		—	
1 „ glycol . ..	—		12·5	10·5	—		—		12·4	10·2	12·7	10·3	12·6	10·3
1 „ glycerol ..	—		17·3	14·4	—		—		17·5	14·5	17·7	14·7	—	
1 „ acetaldehyde	—		—		—		—		12·7	9·3	—		—	
1 „ acetone ..	—		—		—		—		13·0	10·0	—		—	
½ „ ether.. ..	—		—		—		—		11·9	—	—		—	
½ „ paraldehyde	—		—		—		—		16·3	Salted out	—		—	
1 „ ammonia ..	7·1	6·9	—		—		4·8	3·7		—	—		—	

Proportion of added substance.	KCl	NaCl
½ gram-mol. glucose	16·7*	16·0
½ „ α-methyl glucoside	18·8	18·3
½ „ cane-sugar	27·9	27·9
½ „ raffinose	39·5	39·1
½ „ melibiose	30·6	29·7

Proportion of added substance.	NaC
1 gram-mol. glucose	29·5
1 „ α-methyl glucoside	33·0
1 „ cane sugar	47·6

* These values were determined at 25° in solutions containing 1 gram-molecular proportion of electrolyte in 50 gram-molecular proportions of water; they have been placed at our disposal by Dr. Glover.

tions; their motility is on this account considerable, especially in the case of the less soluble; it may be supposed therefore that their dissociating effect on the complexes present in water is considerable (compare VI), although the amount of "active water" associated with them is relatively inconsiderable. If the proportion of hydrone actively associated with the hydrolyst and hydrolyte be reduced to a minimum by the constant intrusion of such molecules between the molecules of solute and solvent, the effect they produce in diminishing solubility, in reducing electrolytic conductivity (a reciprocal process in which solvent and solute are equally concerned) and in depressing hydrolytic activity should be relatively great.

The sugars are presumably somewhat immobile molecules in solution but it is probable that they are associated with a not inconsiderable proportion of the "water"—of "water," moreover, which is in a highly active state (water of hydrolation). As the motility of the molecules is very limited, the mechanical influence they exercise is presumably mainly that of mere hindrances; if so, they have little effect in cutting the connexions established between the molecules of hydrone and those of any other solute present in the solution. It may be supposed that they reduce electrical conductivity to a very marked extent, in part, at least, because of the effect they have in reducing the proportion of hydrolated molecules of the electrolyte, this reduction being due mainly to two causes —the one being the presence of a large proportion of hydrone associated in the active hydrol form with the sugar molecules, the other the presence in the free water of an enhanced proportion of active hydrone or hydronol molecules.

The influences pictured have an opposite effect on solubility, both the free water and the hydrone associated with the sugar in the hydrol form being more active than ordinary water as solvent water—to an extent which even enables the sugar, in some cases, to exercise a negative influence in depressing solubility (compare XI).

The apparent lack of effect manifest in the case of the sugars when their influence on hydrolytic activity is considered is therefore presumably a consequence of the fact that their activity as dehydrolating agents is such as to cause an increase in the activity of the acid which suffices to balance the effect produced by their mechanical interference.

To appreciate the reduction of electrical conductivity determined by non-electrolytes, the effect produced by the various substances under consideration in altering the viscosity of water should be taken into account. The alcohols and the sugars, the latter especially, all increase the viscosity of water, as shown in the following table, in which the approximate values are given of weight-normal molecular solutions*:

	Viscosities at 25°.	Fluidities at 25°.
Water	0·0089	1·000
Methanol	0·0096	0·927
Ethanol	0·0098	0·908
Propanol	0·0118	0·754
Glycol	0·0104	0·856
Cane sugar	0·0218	0·408

The haloids and halogen hydrides, as a rule, have the effect of diminishing viscosity to an extent which increases in passing from chloride to iodide; the following are given by Taylor and Ranken (*Proc. Roy. Soc. Edin.*, 1904, xxv., 231) as the values afforded by volume-normal molecular solutions in comparison with those of water at 0°:

	0°.	15°.	25°.
Water	1·000	0·640	0·501
KCl	0·931	0·632	0·502†
KBr	0·911	0·601	0·483
KI	0·854	0·583	0·467
HCl	1·020	0·667	0·529
HBr	0·987	0·650	0·514

* These values are obtained from curves drawn with the aid of the data given by Dunstan (*Trans.*, 1904, lxxxv., 817, 1905, lxxxvii., 11).

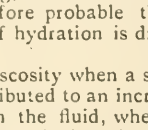
† This value is usually given as rather less than that for water at the same temperature.

The viscosity of a solution of hydrogen iodide would almost certainly be less than that of the bromide. As the viscosity of all the solutions diminishes as the temperature rises far less rapidly than does that of water, it is to be expected that at fairly high temperatures the viscosities of solutions of potassium iodide would be greater than that of water at the same temperature. The three hydrides, however, resemble the corresponding potassium haloids in that conductivity and viscosity bear the same relationship in both series, whilst the apparent hydration values increase, instead of decreasing, as the conductivity rises (compare XVII). It is therefore probable that the condition, as well as the extent, of hydration is different in the case of the three salts.

The increase in viscosity when a substance is dissolved in water may be attributed to an increase in the proportion of hydrol present in the fluid, whether in the free state either as hydrone or as hydronol or combined in the form of hydrolated molecules of the solute (S), thus:—

$$H{\cdot}OH \qquad H_2O{<}^{H}_{OH} \qquad (S){<}^{H}_{OH}$$

From this point of view, the increase in the viscosity produced by the monohydric alcohols may be regarded as mainly due to an increase in the activity of the water (cases 1 and 2), whilst in sugar solutions case 3 also comes largely into operation (compare XIII). The diminution in viscosity in the case of haloids may be ascribed to the formation of a large proportion of relatively inert hydronated molecules of the polymethylene type, for example:



If, in the case of iodides, a larger proportion of such molecules were formed than in the case of the bromides or chlorides; if a similar difference also obtained between bromides and chlorides: the proportion of active molecules would be smallest in the case of the iodide and greatest in the case of the chloride. But in such an event, in the case of the iodide, there would be least and in the case of the chloride most free water present; therefore the iodide would exercise the greatest and the chloride the least effect in influencing hydrolytic change.

From this point of view, electrical conductivity is not a direct measure of any single or simple effect—of the number of molecules activated—but like other properties a measure of the algebraic sum of a complex series of effects.

The relatively small effects produced by the lower alcohols and ammonia may also be explained as a consequence of the manner in which they undergo hydration. It appears to be not improbable that such compounds exist in solution as "hydrates" closely allied in structure to those of the complex molecules which are chief constituents of liquid water. This point of view, in fact, is one which we incline to regard as of importance, as that from which an explanation may be given of not a few of the differences manifest in the behaviour of aqueous solutions.

There are various directions in which it is desirable to extend the experiments to test the sufficiency of the explanations suggested; at present we are mainly concerned in insisting that, however regarded, the phenomena are exceedingly complex in character and that an apparent agreement between hypothesis and fact in a single case must not be allowed to mislead judgment; no stronger proof of this can be given than is afforded by the cases discussed in this communication, as although no noticeable effect is produced on hydrolytic activity by non-electrolytes such as the sugars, their presence causes an extraordinary diminution in electrolytic activity coupled with an increase in viscosity.

RECENT ADVANCES AND PROBLEMS IN CHEMISTRY.*

By Prof. EMIL FISCHER, Professor at Berlin University.

Your Majesty, Gentlemen,—At no single period in the past has there been so strong a tendency to examine critically all branches of knowledge, and, if necessary, to make fundamental alterations in our conclusions, as there is at the present time. This is true of all the natural sciences. Owing to new methods of observation our actual knowledge has made extraordinary advances in the last ten years, and in view of the new phenomena the old theories appear far too restricted. Even the foundations of our knowledge appear to a certain extent to be in need of modification.

Thus the advances in Physics are forcing upon us ideas which are not in harmony with the old theory of mechanics, although this was regarded by thinkers like Hermann von Helmholtz, Heinrich Hertz, and Lord Kelvin as unassailable.

The elements of chemistry are in similar case. Owing to the discovery of radium and similar substances we are led to the assumption that the chemical elements are not unalterable, and that their atoms are not indivisible.

In the biological sciences the advance is still more rapid. Comparative anatomy, the physiology of animals and plants, the theory of evolution, microbiology, and almost all branches of medicine are rapidly advancing from a practical point of view, while theories are changing equally quickly. Also the semi-historical natural sciences, geology, palæontology, anthropology, and astronomy are sharing in the general progress.

It is thus at a time of great activity that the "Kaiser Wilhelm Gesellschaft" has been founded, and its main object is the establishment and maintenance of Institutes for Research.

Naturally we scientific men greet this new departure with great enthusiasm, and I consider myself highly honoured in that I have been permitted to be the first to express our gratitude for it.

Nobody could maintain that experimental science has suffered from neglect in Germany. A glance over the history of science in the nineteenth century shows the contrary. It reveals a long series of brilliant scientific discoveries which have been made in our country. Moreover, the trades and industries closely connected with science, like the chemical industries, electrotechnics, the extraction of metals, the fermentation industry, and last but not least agriculture, have seen a development amongst us which other nations often begrudge us.

A criterion of the success of scientific research is afforded by the awards of the Nobel Prize, which is conferred by perfectly independent corporations in Sweden.

Four weeks ago the Nobel Prize for chemistry was awarded to Germany for the sixth time, which makes 60 per cent of all the chemistry prizes given. In the same period of time German physicists received two and a-half prizes, and German doctors three and a-half. Unfortunately Dr. Alfred Nobel did not make provision for the other sciences.

But the researches rewarded by these prizes belong mostly to the nineteenth century. Since then the conditions have somewhat altered. It is well known that most German scientists are also teachers in a High School. At our High Schools in the course of the last ten years a practical course of instruction has been evolved which gives all students an opportunity of acquiring a thorough grounding in experimental work, and which also provides our industries with a supply of scientifically trained officials. But this course of work entails a greater strain on the teachers than is desirable or even endurable for the creative activity of the investigator.

In a modern laboratory there is as much pressure as in a fairly large factory or a business house, and in the daily wear and tear the teachers too easily lose tranquillity of mind and a wide outlook on the great problems of science. This difficulty has been most felt among teachers of chemistry, to which class I belong. It is not therefore merely by accident that in our circle there has recently been a great demand for new Institutes which would be free from the burden of teaching, and which would provide perfect quiet for experimental research.

But, in spite of support from an industry which was prepared to make considerable sacrifices, all our efforts have not led to the desired result, and we were on the point of reluctantly giving up the scheme when His Majesty's idea of appealing to the generosity of our compatriots seemed to us like help sent from heaven.

Instead of one Chemical Institute maintained by the whole empire, as we had planned, chemists may now hope shortly to be in possession of two Research Institutes where gifted men will have abundant opportunity to give full play to their spirit of investigation unhampered by any other duties. Probably the younger generation of chemists will specially profit by it. I am now thinking of men who are at present assistants or demonstrators in High School laboratories, and who, owing to their compulsory duties, can spare time for research only by dint of working exceedingly hard.

Mutatis mutandis, the same may be said for other sciences as for chemistry, and it is specially true of new branches of knowledge for the investigation of which the heavily burdened organisation of teaching laboratories offers no opportunity.

The advantage which foreign countries, especially the United States, have obtained owing to the possession of such institutes may again be pointed out. If the hopes we all have of the new Institute are fulfilled, in the future there will be no lack of Nobel Prizes for Germany, and we may hope to maintain the proud position we have hitherto held in research.

Moreover, we see that it is not a question of honour only, but also of decided material advantages, when we reflect on the close connection between progress in research and political economy. It does not lie within my province to put before you figures and economical considerations giving details of these relations. But, on the other hand, I may act as your guide on a flying visit to my own science. It will give me opportunities to point out the diversity of the problems and their importance in the different regions of industrial life in the light of the newest achievements.

As has already been said, our conception of a chemical element has been somewhat altered by the discovery of radium, the first element to be discovered by a woman. We now know more than two dozen similar substances, the so called radio-active elements, and we are aware that they decay spontaneously, thus being capable of undergoing elementary transformations.

At first Germany took only a small part in these important investigations, although the clue to the discovery of radium came from the Röntgen rays. The reason for this is that Germany possesses no raw material for the preparation of radium, and most German investigators have not the means to buy the expensive element. This lack was particularly regrettable as radium was successfully applied in medicine for different purposes.

The discovery recently made by Prof. Otto Hahn in the Chemical Institute of this University is all the more gratifying. For several years he has been studying the transformation products of thorium, which is extensively used in the manufacture of gas mantles. He has thus discovered several radio-active elements, and has named the most important mesothorium. He has also succeeded in working out a method of obtaining this mesothorium from the valueless residues of the manufacture of thorium. I am able to show you a specimen of Hahn's preparation. It is the bromium compound of mesothorium, a white salt which emits the same penetrating rays as the corresponding

* A Lecture, illustrated by experiments, delivered in the presence of His Majesty the Kaiser on the occasion of the founding of the Kaiser-Wilhelm Society for the Advancement of Science, on January 11, 1911, at Berlin.

radium salt. With regard to the power of radiation of this preparation it corresponds to 100 mgrms. of pure radium bromide, while it has cost only a third as much. Nevertheless it is not cheap, for 11,000 marks was paid for this small quantity. Thanks to a donation from Dr. von Böttinger of Elberfeld, the Berlin Academy will in a few months' time possess 250 mgrms. of it, and will lend it to German investigators. Every year from the useless residues of the manufacture of thorium in Germany an amount of Hahn's preparation can be obtained corresponding to more than 10 grms. of pure radium bromide. This is about as much as the total amount of radium salts yet obtained.

This discovery will compensate for the lack of radium from which Germany has hitherto suffered.

The sphere of experimental chemistry has been very greatly widened in the last ten years by the possibility of easily obtaining very high and very low temperatures. The former is effected by electric furnaces, by means of which 3000° is easily reached. The latter are obtained by cooling with liquid air. This can now be bought in Berlin at the cost of a medium wine, *i.e.*, 1·75 m. per litre. This we owe to your Majesty, who has allowed Prof. von Linde of Munich to set up here one of his large machines for iquefying the air. In order to show how indispensable it has become to us I may mention that in this University Institute some litres of it are used every day for scientific purposes.

Liquid hydrogen, the temperature of which lies about 60° lower, is even more useful. It boils at −252·6°, *i.e.*, only 20·4° above the absolute zero. Liquid hydrogen cannot be bought in Berlin, and it is usually not to be obtained here. However, I can show you a specimen which comes from the Physical Institute of the University of Leipzig, where it was prepared this morning, and then sent here with great care. We will pour a specimen from the specially constructed containing vessel into a transparent glass vessel, and I will demonstrate the low temperature by immersing in it a glass tube closed at the bottom. On taking the glass tube out it is seen to be filled with a white mass like snow, which is the frozen air; however, when it is removed from the cooling liquid it melts in a few seconds.

The rest of the liquid hydrogen which has been left in the receptacle will also be used for scientific purposes. For at the end of my lecture it will go to the University Institute of Physical Chemistry, in order to be used this evening and during the night by Prof. W. Nernst for heoretically important researches on the specific heat of the elements in the neighbourhood of the absolute zero.

When the Kaiser Wilhelm Institute of Chemistry is in working order we hope not to have to send to Leipzig for liquid hydrogen.

Liquid hydrogen was first prepared about twelve years ago by Prof. Dewar in the laboratory of the Royal Institution in London. But he was able to perform this difficult experiment only owing to the abundant means placed at his disposal by the great benefactor of chemistry, Dr. Ludwig Mond. Moreover, Dr. Mond has not forgotten his German fatherland and German science. The University of Heidelberg, where he studied, received from him a bequest of a million marks for chemical and physical investigation, and he also contributed several years ago 200,000 marks to the Chemical Institute planned by us.

Inorganic chemistry which thirty years ago was regarded as thoroughly investigated has taken a new lease of life owing to these new agents, *e.g.*, high temperatures, strong electric currents, &c. I propose now to point out some technically important processes, and shall begin with experiments to make use of the nitrogen of the air for the preparation of valuable nitrogen compounds.

The direct conversion of the air into nitric acid by powerful electric discharges has reached the stage of a major industry. In Norway, in the neighbourhood of a large waterfall, a huge factory has been started by German manufacturers in conjunction with Norwegian engineers, financed by German and French capital.

Artificial saltpetre is already on the market, and German colour manufacturers will obtain a considerable amount of the nitrous acid they require from the same source.

A short time before the very original method of preparing calcium nitride from calcium carbide and atmospheric nitrogen, which was worked out by Prof. A. Frank and Dr. N. Caro, of Charlottenburg, came into use.

And yet another method has been described, by which atmospheric nitrogen has been made to combine directly with hydrogen to give ammonia. For by the ingenious application of the principles of physical chemistry, Prof. Haber, of Karlsruhe, has overcome the difficulties which have hitherto stood in the way of the practical use of the synthesis.

The well-known Badische Anilin und Soda-Fabrik at Ludwigshafen a.-Rh. has taken up his patents and so far perfected the method technically that probably we shall soon have synthetic ammonia on the market.

The more numerous such methods are, and the keener the competition among them, the better it is for the consumer. In the above-mentioned cases this has a special significance because the greater quantity of the nitrogen compounds is used in agriculture as artificial fertilisers.

In the opinion of experts German agriculture could easily employ twice or even three times as much nitrogen compounds as at present, if the price were correspondingly lowered. Possibly farmers would thus be able to increase their crops to such an extent that Germany could be independent of foreign countries as regards agricultural products. Thus a problem of great national importance is put before chemical industry.

The last-named process, the synthesis of ammonia, has the advantage that it requires no electricity, but only heat, or, in other words, fuel, of which Germany has an abundant supply. It is, moreover, noteworthy that its profitable working depends upon the price of hydrogen, which in conjunction with the cheap atmospheric nitrogen serves as the raw material. The problem of preparing cheap hydrogen has already been solved by chemical industry in consequence of the stimulus offered by aeronautics. This confirms the experience that all commercial activity is interdependent, and that improvements in one region may have a very considerable influence upon very different branches.

A similar connection of mutual benefit exists between scientific chemistry and the preparation of metals. The preparation of gold, silver, and copper has been wonderfully simplified by the application of electrochemical methods. The study of metallic alloys and the cheap preparation of metals formerly difficult to obtain, such as chromium, tungsten, manganese, vanadium, and tantalum, has been put to good use in the steel industry and in electrotechnics.

And—not to forget the latest novelty in this region—I have here a new sort of iron, the so-called electrolytic iron. It was prepared by the Langbein-Pfannhauser Works in Leipzig by a method which was discovered by Professor Franz Fischer working in the Berlin University Institute; in this process the metal is separated by a salt of iron by means of an electric current. Besides solid plates up to 5 mm. thick which can easily be rolled and drawn out into wire, you see here a shining lamina which is not polished, but was separated directly from the electrodes in this state; also a spirally wound iron tube without a seam which was separated in the same way on a lead mould.

This iron is different from all known commercial sorts because of its exceptional purity, in consequence of which it also possesses certain other physical properties. Thus it becomes magnetic much more quickly and also loses its magnetism very rapidly. Hence it can be used to make very effective electromagnets. This electromotor of the ordinary type standing before you had originally a horse power 0·5; when the old electromagnets had been

replaced by electrolytic iron its capacity rose to 1·25. This new iron will be of great importance in the construction of electromotors.

Nowadays our material comfort depends considerably upon the consumption of fossil fuels—coal and lignite. Later generations, however, will not spare us the reproach that we have been wickedly lavish with this valuable material. For if steam is produced by heating with coal in the ordinary way and then transformed into mechanical motion by steam engines, more than 85 per cent of the energy originally in the coal is lost. But this loss may be considerably diminished by a suitable chemical treatment of the coal. For if the coal is first converted into combustible gases, the so-called power gas, and then burnt in gas motors, the yield of effective power can be increased to three times that of the steam engine. Valuable ammonia and tar are obtained as by-products, and undoubtedly the methods at present used for the preparation of power gas are capable of alteration and improvement in many respects. I suppose therefore that in the centres of the coal industry special institutes—perhaps modelled on the Kaiser Wilhelm Gesellschaft—will appear, and in them this important question will be investigated with all the means at the disposal of science and in the closest connection with practice.

The fossil fuels which were originally derived from the vegetable kingdom also form a link between mineral and organic substances. The chemistry of the latter greatly surpasses mineral chemistry in the multiplicity of its methods and its results. This is not remarkable, for it includes all the complicated chemical substances which occur in the plant and animal body. The number of thoroughly investigated organic compounds may be estimated at 150,000, and each year is increased by 8000 to 9000. It may therefore be calculated that at the end of this century organic chemistry will include as many individuals as the living world—the animal and vegetable kingdoms together.

This rapid increase is the work of organic synthesis from a few elements, of which carbon is the chief; it builds up in a marvellous manner all these combinations, just as an architect from the same bricks produces different kinds of buildings.

Organic synthesis is a child of Berlin. It began here in the Niederwallstrasse eighty-two years ago with the artificial preparation of urea by Friedrich Wöhler. It has been mostly carried out in Germany. Now-a-days it does not hesitate to try to produce the most complicated constituents of the living organism. I will show you this in the three classes of substance which are of the greatest importance in the living world—fats, carbohydrates, and albuminoids. The synthesis of fats was performed by M. Berthelot in Paris two generations ago. The first artificial carbohydrates—grape-sugar, fruit-sugar, &c.—saw the light twenty years ago in Wurzburg. And the methods of the artificial building up of albuminous substances have been worked out in the Berlin University Institute during the last ten years. Hence I am in a position to show you one of these products. It is the most complicated substance which synthesis has yet produced, and has such a long name that I do not dare to pronounce it here. The quantity of the preparation is very small, and as you will see again presently the vessels of experts generally differ from those of the manufacturer in their remarkable smallness. This difference is of the same order of magnitude as the difference between the possessions of these two classes of men.

Nevertheless, the artificial albuminous substance like Hahn's preparation is not cheap. The raw materials which are necessary for its preparation cost about 1000 marks, and the labour involved must be estimated at a still higher figure. Thus it is not adapted for food. It is only a curiosity, but a substance which is a curiosity to-day may be useful to-morrow. Chemistry has already provided many examples of this.

(To be continued),

BEARING OF THE SOLVATE THEORY OF SOLUTION.*

By HARRY C. JONES.

(The evidence for the solvate theory of solution has bee furnished through investigations carried out in this laboratory, largely with the aid of grants from the Carnegie Institution in Washington).

The evidence for the solvate theory of solution, which has been furnished in this laboratory as the result of somewhat more than a dozen years of investigation, has recently been brought together, and briefly discussed (*Zeit. Phys. Chem.*, 1910, lxxiv., 325). The evidence is so unambiguous and convincing that ions and some molecules combine with more or less of the solvent that it can now be accepted as a fact of science.

This, however, raises a number of questions, What relation does the solvate theory of solution bear to the theory of electrolytic dissociation?

Does the solvate theory help us to explain any of the apparant discrepancies in the theory of electrolytic dissociation? Does the solvate theory help us to explain the facts of chemistry in general and of physical chemistry in particular? Why is the nature of solution so important, not only for chemistry but for science in general.

The Solvate Theory and the Theory of Electrolytic Dissociation.

When Arrhenius proposed the theory of electrolytic dissociation the question was not even raised as to the condition of the ions in the solution except that they behave as if they existed independent of one another in solution. The theory simply said that molecules of acids, bases, and salts in the presence of a dissociating solvent like water break down to a greater or less extent into charged parts called ions; the cations or positively charged parts being electrically equivalent to the anions or negatively charged parts. The cations are usually simple metallic atoms carrying one or more unit charges of positive electricity. The cation might, however, be more or less complex, as illustrated by ammonium and its substitution products. The anion is usually complex, consisting of a larger or smaller number of atoms. It may, however, be an atom carrying negative electricity as in the case of the halogen acids and their salts.

The degree of dissociation is determined by the nature of the acid, base, or salt. Strong acids and bases are greatly dissociated. Indeed, the degree of dissociation determines their strength. Nearly all of the salts are strongly dissociated compounds; there being, however, some exceptions, as, notably, the halogen salts of mercury, cadmium, and zinc. There are, however, considerable differences in the amounts to which salts in general are dissociated at the same dilution.

The quantitative evidence furnished by Arrhenius and others for the theory of electrolytic dissociation is so convincing that few chemists of any prominence who have carefully examined the evidence have ever doubted the general validity of the theory, and the theory has become substantiated by such an abundance of subsequently discovered facts that it has now become a law of nature and a fundamental law of chemical science.

Arrhenius saw and pointed out clearly the importance of ions for chemistry, and Ostwald and his pupils have shown that chemistry is essentially a science of the *ion*, molecules for the most part being incapable of reacting chemically with molecules, and Nernst has shown that the ion is the active agent in all forms of primary cells.

The theory of electrolytic dissociation, as already stated, does not raise the question as to the relation between the ion and the solvent. At the time that the theory was proposed chemists did not know, and probably had no means of finding out, whether the ion is or is not combined with

* *American Chemical Journal*, 1911, xlv., 146.

the solvent in contact with it. The solution of this problem remained for subsequent work.

Some of the many lines of evidence that ions and certain molecules are combined with a larger or smaller number of molecules of the solvent, and in many cases with a very large number of molecules of the solvent, as has already been stated, have recently been discussed briefly by myself in an article in the *Zeitschrift fur Physikalische Chemie* ("Evidence Obtained in this Laboratory during the Past Twelve Years for the Solvate Theory of Solution," *Zeit. Phys. Chem.*, 1910, lxxiv., 325).

The amount of the solvent combined with an ion is primarily a function of the nature of the ion or ions in the solution. It is, however, conditioned very largely by the dilution of the solution and also by the temperature.

The evidence, some of which is given in the paper referred to above, and the remainder in other publications, of the results of investigations carried out in this laboratory during the past dozen years, shows that the power of the ions to combine with the solvent is by no means limited to water and aqueous solutions, but is a property of solutions in general ("Conductivity and Viscosity in Mixed Solvents," by H. C. Jones and co-workers; Carnegie Institution of Washington, Publication No. 80). The alcohols, acetone, glycerol, &c., combine with certain substances dissolved in them, and it seems more than probable that all solvents combine with the dissolved substances to a greater or less extent. In a word, we do not have simply a theory of hydration, but a theory of solvation in general, which is an essential part of any generalisation which would take into account the facts presented by solution.

The solvate theory of solution has been regarded in some cases as a rival of the electrolytic dissociation theory of solution, if not directly antagonistic to it. Such is not at all the case. The solvate theory begins where the theory of electrolytic dissociation ends. The latter gives us the ions from molecules, and the former tells us what is the condition of the ions in the presence of a solvent after they are formed.

The solvate theory of solution, then, simply supplements the theory of electrolytic dissociation, and both must be taken into account if we ever wish to understand the phenomena presented by solution.

Does the Solvate Theory Help to Explain any of the Apparent Exceptions to the Theory of Electrolytic Dissociation?

Given the theory of solvation in solution together with that of electrolytic dissociation, the first question that arises is, does the former really aid us in explaining the phenomena presented by solutions?

Shortly after the theory of electrolytic dissociation was proposed, it was recognised and repeatedly pointed out that after all it is only a theory of "ideal solutions"; *i.e.*, very dilute solutions. It was shown not to be able to explain many of the phenomena presented by even fairly concentrated solutions. Indeed, it often could not deal quantitatively with the very solutions with which we work in the laboratory.

The explanation of this shortcoming was not fully seen, and an analogy was resorted to. It was pointed out that the laws of Boyle and Gay-Lussac for gases hold only for "ideal gases," *i.e.*, dilute gases, but do not hold for any gases of considerable concentration.

It was stated that the gas laws when applied to solutions could not be expected to hold more generally than when applied to gases, and there the matter was allowed to rest.

In the early days of the theory of electrolytic dissociation it was, however, pointed out that we have a fairly satisfactory explanation of why the simple gas laws do not hold for concentrated gases, and this was expressed in the equation of Van der Waals, while no analogous explanation was offered in the case of solutions.

That this point was well taken is obvious to anyone. A theory of solution to be of the greatest value must be applicable to all solutions regardless of the nature of the substance, regardless of the nature of the solvent, and regardless of the concentration of the solution.

The explanation of these apparent exceptions to the theory of electrolytic dissociation presented by concentrated solutions has been furnished by the solvate theory. We now know that for solutions in general a part of the solvent is combined with the dissolved substance. While the amount of the solvent combined with any one ion is greater the more dilute the solution, at least up to a certain point, the total amount of the solvent in combination with the dissolved substance is greater the more concentrated the solution.

That the amount of combined solvent may become very great, even relative to the total amount of solvent present, can be seen from the following facts:—In a normal solution of calcium chloride about two-fifths of the total water present is combined with the dissolved substance. In a three normal solution of calcium chloride about five-sevenths of the total water is combined.

In the case of a normal solution of aluminium chloride in water about five-eighths of the water present is combined with the dissolved substance, while in a two normal solution about five-sixths of the water present is in a state of combination ("Hydrates in Aqueous Solution," by H. C. Jones and co-workers, Carnegie Institution of Washington, Publication No. 60).

What we suppose to be a normal solution of calcium chloride is therefore more than one and one-half times normal, while what we suppose to be a three normal solution is in reality more than eight times normal. In the case of aluminium chloride what we suppose to be a normal solution is more than twice normal, while what we prepare as a twice normal solution is about twelve times normal.

These few facts taken from thousands of a similar character show that even fairly concentrated solutions are much more concentrated than we would suppose from the method of their preparation, while very concentrated solutions are many times more concentrated than without the facts of solvation we should be led to think.

The general conclusion is that even fairly concentrated solutions are much stronger than if no solvation occurred, and are much more concentrated than we are accustomed to consider them from the amount of substance added to a given volume of the solution—more or less of the water present being in combination and only the remainder playing the *rôle* of solvent. Without the theory of solvation we have hitherto regarded all the water present as playing the *rôle* of solvent.

We should therefore not expect the laws of gases to apply to such solutions when we had no idea what their true concentration was. Now that we know their concentration we find that the laws of gases are of as general applicability to solutions as to gases, holding not simply for dilute solutions, but also for concentrated.

The theory of electrolytic dissociation, supplemented by the theory of solvation, is then not simply a theory of dilute or "ideal" solutions, but a theory of solutions in general.

Does the Solvate Theory Aid us in Explaining the Facts of Chemistry in General and of Physical Chemistry in Particular?

To answer this question at all fully would lead us far beyond the scope of this paper. A few facts bearing upon this question can, however, be taken up. Take, for example, the action of the hydrogen ion, both in the formation and the saponification of esters. In the presence of the alcohols the hydrogen accelerates greatly the velocity with which an ester is formed, while in the presence of water it causes the ester to break down into the corresponding acid and alcohol.

In terms of ordinary chemical conceptions it is difficult, not to say impossible, to interpret these reactions—the hydrogen ion under one set of conditions undoing what under other conditions it effected.

In terms of the solvation theory these reactions admit of a very simple interpretation. While the hydrogen ion is not strongly solvated, yet work in this laboratory has shown that all ions are more or less solvated. In the presence of alcohol the hydrogen ion therefore combines with a certain amount of this solvent. The hydrogen ion plus the alcohol combined with it unites with the organic acid, forming complex alcoholated ions, which then break down forming the ester.

On the other hand, the hydrogen ion in the presence of water combines with a certain amount of this solvent. The hydrated hydrogen ion together with the water united with it combines with the ester, forming a complex hydrated ion, which then breaks down into the corresponding acid and alcohol, setting the hydrogen ion free again.

For a fuller discussion of this reaction see the paper by E. Emmet Reid (*Am. Chem. Journ.*, 1909, xli., 504).

A reaction analogous to the above is that of hydrogen ions on amides in the presence of water, on the one hand, and of alcohol on the other. In the presence of water the hydrated hydrogen ion combines with the amide, forming a complex hydrated ion, which then breaks down, yielding ammonia and acid, the ammonia, of course, combining with the acid. In the presence of alcohol the alcoholated hydrogen ion combines with the amide, forming a complex alcoholated ion, which then breaks down into ammonia and the ester of the acid in question.

Hydrogen ions in a mixture of water and alcohol, which would contain both hydrated and alcoholated hydrogen ions, give both reactions simultaneously; but as Reid has pointed out, in the presence of an equal number of molecules of water and alcohol, the tendency of the hydrogen ion to hydrate is greater than the tendency to form alcoholates, and under these conditions the first reaction proceeds relative to the individual reactions much more rapidly than the second (*Am. Chem. Journ.*, 1909, xli., 509).

A very large number of types of reactions could be discussed illustrating this same point; *i.e.*, the value of the solvate theory in interpreting chemical reactions.

When we turn to physical chemical processes the solvation of the ions has to be taken into account at every turn. The velocities of the ions are, of course, a function of the degree of their solvation, and the behaviour of the ions both chemically and physically is a function of their velocities. The effect of dilution, and especially of temperature, on reaction velocities is largely a question of the velocities of the ions present, which in turn are a function of the degree of their solvation.

In determining the actual concentration of a solution the amount of the solvent combined with the ions must be taken into account, as has already been pointed out, and without knowing the actual concentrations of solutions quantitative chemistry would be impossible.

The solvate theory has thrown a flood of light on the whole subject of the conductivity of solutions, or the power of the ions to carry the electric current. It has shown us why the conductivity of lithium salts is less than that of sodium and potassium, notwithstanding the fact that the lithium ion is much smaller and lighter than the atom of sodium and potassium. We now know that the lithium ion is much more hydrated than the ions of sodium and potassium, and the mass of the moving ion is really much greater than that of sodium or potassium.

When we come to the temperature coefficients of conductivity, the solvate theory has enabled us to interpret results which, without its aid, would be meaningless. We now know why ions with the greater hydrating power have the larger temperature coefficients of conductivity. We know why ions with the same hydrating power have approximately the same temperature coefficients of conductivity, and why more dilute solutions have larger temperature coefficients of conductivity than more concentrated (Jones, *Am. Chem. Journ.*, 1906, xxxv., 445), and we could multiply examples almost without limit, did space permit, of the effect of the solvate theory on physical chemistry.

Why is the Nature of Solutions of such Vital importance not only for Chemistry but for Science in General?

The fact is well recognised that modern physical chemistry has reached out into nearly every branch of science, and has had an important influence on many of them. The question arises, Why is this the case? The answer is that physical chemistry is primarily a science of solutions.

This answer may not at first sight appear to be self-evident, but a moment's thought will show its general correctness. The whole science of chemistry is primarily a science of solutions in the broad sense of that term. By solutions is meant not simply solutions in liquids as the solvent but solutions in gases and in solids as well, and not simply solutions at ordinary temperatures but also at elevated temperatures.

If we think of chemical reactions in general we will realise what a small percentage of them take place out of solution. Therefore the nature of solution is absolutely fundamental for chemistry. This applies not simply to general chemistry, including the chemistry of carbon, but also to physiological chemistry, which deals almost entirely with solutions in one solvent or another.

When we turn to physics we find solutions not playing as prominent a *rôle* as in chemistry, but, nevertheless, coming in in many places. The primary cells, secondary cells, electrolysis, polarisation, diffusion, viscosity, surface-tension are all phenomena in which the physicist is interested, and all depend for their existence upon solution.

When we turn to the biological sciences we find that solution is almost as important as for chemistry. Take physiology; here we have to deal very largely with solution in the broad sense of the term. The same remark applies to physiological botany, and solutions are very important for both animal and vegetable morphology, especially in their experimental developments. Bacteriology is fundamentally connected with solutions, and pharmocology is based upon solutions either without or within the body of the animal.

Solution in the broad sense is as fundamental for geology as for chemistry. The igneous rocks were solutions of one molten mass in another, and sedimentary deposits came down for the most part from solutions in water. The minerals crystallised out from solutions, and solutions of various substances, such as carbon dioxide, are to-day weathering the rocks and continually changing the appearance of the face of the globe.

An examination of facts such as those referred to above will show the truth of the statement that the relation of physical chemistry to solutions is the prime reason why physical chemistry is so closely related to so many other branches of natural science.

This alone would show the importance of a true and comprehensive theory of solutions, not alone for physical chemistry but for the natural sciences in general.

Physical Chemistry Laboratory,
Johns Hopkins University,
October, 1910.

Royal Institution.—On Tuesday next, March 21, at 3 o'clock, Dr. M. Aurel Stein delivers the first of a course of three lectures at the Royal Institution on "Explorations of Ancient Desert Sites in Central Asia." The Friday Evening Discourse on March 24 will be delivered by Sir David Gill on "The Sidereal Universe," on March 31 by Prof. H. S. Hele-Shaw, on "Travelling at High Speeds on the Surface of the Earth and Above it," and on April 7 by Prof. Sir J. J. Thomson, on "A New Method of Chemical Analysis."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY,

Ordinary Meeting, February 23rd, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Transmission of Flagellates living in the Blood of certain Freshwater Fishes.*" By Miss M. Robertson, M.A.

"*Report on the Separation of Ionium and Actinium from certain Residues, and the Production of Helium by Ionium.*" By B. B. Boltwood, Ph.D.

At the end of 1907 the Royal Society lent to Prof. Rutherford certain actinium residues, which were part of the material remaining after the separation of the radium by Messrs. Armet de Lisle, of Paris, from uranium residues acquired by the Royal Society. These residues, in weight 20 kilogrms., contained a large quantity of lead, and were a very heterogeneous mixture of elements. A preliminary examination made by Prof. Rutherford showed that actinium was present, and also a small quantity of radium. The amount of ionium, however, was much less than the theoretical amount to be expected if all of it had been removed with the actinium. The preliminary work of concentration was done by Messrs. Tyrer and Co., under the direction of Prof. Rutherford and Mr. Greenwood. This material was given to the writer for further concentration, and the paper contains an account of the methods employed in the separation of the actinium and ionium.

The ionium was finally obtained mixed with 1·8 grms. of thorium oxide. The activity of this oxide, due to the ionium it contained, was about 3000 times that of an equal weight of uranium oxide. By counting the α-particles from a thin film by the scintillation method, the amount of ionium present with the thorium was found to be equal to the amount in equilibrium with 5·3 mgrms. of radium in a radio-active material. The actinium was finally concentrated to about 10 grms. of material, which gave a final activity about 20,000 times that of uranium oxide. It was estimated that the amount of actinium separated was equivalent to the amount in equilibrium with 30 mgrms. of radium in a mineral.

Special experiments were made to test whether ionium was transformed into helium. The presence of helium was determined by its spectrum, and the volume produced was measured. The investigation showed that helium is produced by ionium as well as by all other products which emit α-rays.

"*Secondary Rays produced by β-Rays.*" By J. A. Gray, B.Sc.

Secondary γ-rays are produced in different materials by the β-rays of RaE, the greater in amount the greater the atomic weight of the radiator. The γ-radiation observed from a preparation of RaE can be greatly increased by a suitable disposition of the active matter and apparatus.

"*Specific Heat of Water.*" By W. R. Bousfield, M.A., K.C., and W. Eric Bousfield, B.A.

The object of this investigation was to obtain a basis curve for the specific heat of water, for comparison with specific-heat curves of aqueous solutions. Former observers using different methods have obtained widely varying curves; thus for the specific heat of water at 80° in terms of the 15° calorie, the following figures have been given, showing differences of 1 per cent:—Barnes, 1·0014; Regnault, 1·0081; Lüdin, 1·0213.

For the value in joules of the 15° calorie the following have been found:—Joule, 4·174; Griffiths, 4·198; Barnes, 4·184.

The first part of our investigation is concerned with the determination of the mechanical equivalent of heat in terms of the mean calorie from 13° to 55°, by a method of continuous flow calorimetry. Mercury thermometers were used which could be read to 0·005°. An interval of 40° was taken, so that an error of 0·01° would not vitiate the result by more than 1 in 4000. Through a Dewar vessel containing about 3 litres of water, in which was an electric heater, there was passed a current of water, entering at about 13° and passing out at about 55°. The vessel was immersed in a bath kept at same temperature as contents of vessel. The top of the vessel was closed by a platinum box kept 10° higher.

The electric heater, and the resistance used in series with it for determining the current by help of a battery of standard cells, were of novel type. Each consisted of a spiral glass tube of small bore into the ends of which are sealed platinum electrodes. The tube is connected with a thermometer tube so that the spiral forms a thermometer bulb. By calibrating the resistance against the reading of this thermometer tube, the resistance is accurately known, even when a current is passing. This type of resistance enabled us to surmount a difficulty apparently never considered by previous investigators. We have found that when a heavy current passes through an ordinary standard resistance, the resistance of the standard depends not only on temperature but also upon strength of current. This effect may be conveniently called the "thermoid" effect. We believe a liquid mercury resistance is free from any such effect.

The continuous flow experiments gave for distilled water $J^{15}_{25} = 4{\cdot}182$. To get the curve for J from 0° to 80°, a weighed quantity of water was heated from 0° to 80° by stages which gave J^{13}_{0} J^{17}_{13} J^{25}_{17} J^{80}_{25}, the mean specific heats over the intervals. For this purpose the capacity of the calorimeter was obtained from the value of J^{25}_{18} previously determined, and a separate research on the specific heat of glass was carried out in order to obtained the variation of capacity with temperature. From these an equation for the value J^{θ}_{0} was obtained, and then the value of J from point to point, from the equation—

$$J = \frac{d}{d\theta}(\theta J^{\theta}_{0}).$$

We thus obtain $J = 4\ 2085 - 0{\cdot}003022\theta + 0{\cdot}00007833\theta^2 - 0{\cdot}0000004490\theta^3$, which gives for the value of the 15° calorie 4·179. The resulting curve corresponds closely with that obtained by Lüdin by the method of mixtures, and differs considerably from that obtained by Barnes by continuous flow with platinum thermometry.

"*Measurement of Specific Inductive Capacity.*" By Prof. C. Niven, F.R.S.

The paper contains an account of work undertaken to determine the specific inductive capacity of liquids by the method of resonance. The frequencies of the discharge of condensers with air and with liquid as dielectric were compared by the cymometer and dielectric constants of the liquids deduced. With some liquids, notably with water, the question is complicated by the conductivity of the liquid. The conditions of discharge through a conducting liquid are therefore first determined, and the condition of resonance between the two resonating systems found. This is shown to be of a simple character, reducing practically to what it would be if the conduction through the liquid were neglected.

In some cases, water for example, it is impossible to set up oscillations directly; but by interposing in the circuit of the condenser another of considerable capacity, the oscillations may be obtained. When the capacity of this interposed condenser is relatively very large, it has no appreciable effect on the frequency of the oscillations produced, which are thus those of the liquid condenser alone.

Owing to the rapid variation of the specific inductive capacity with temperature, special arrangements had to be made to keep the liquid at a constant temperature while measurements were being made. The results of a number of determinations at different temperatures are given for water and alcohol.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, March 6th, 1911.

Mr. E. Grant Hooper in the Chair.

The following paper was read and discussed :—

"*Industry of Brewing.*" By A. Chaston Chapman.

In this paper the author has confined himself to a consideration of certain of the more striking developments which have taken place in the brewing industry during comparatively recent years, with special reference to the more important improvements which have been introduced during that time in respect of plant and procedure. The heavy fiscal burdens which the industry has been called upon to bear, in conjunction with certain other causes, have combined to produce a state of depression which at first sight might not appear to be favourable to rapid development in the matter of plant and practice, but in many cases it is certain that this very state of affairs has compelled the brewer to instal perfected machinery, and to adopt scientific methods which, under more prosperous circumstances, he might have regarded merely as matters of interest. Dealing with the question of the grinding of the malt, the author referred to the comparatively recent introduction of mills, in which, by means of some mechanical device, the husk is separated from the starchy portion of the grain, so that the latter may be finally ground, leaving the husk almost intact for the purpose of assisting mash-tun drainage. Several of these perfected mills are on the market, and are giving in practice very good results in the direction of increased extract yield. Of course, with perfectly modified and thoroughly mealy and friable malt, these perfected forms of mill possess little, if any, advantage over the ordinary double-roller mills. Using, however, malts such as those with which the brewer has ordinarily to deal, the increased extract yield obtained by the employment of such mills is often considerable. There are very few breweries in the country at the present time where at least an additional pound of extract per quarter could not be got, and this in a 50-quarter brewery, brewing five times a week, would mean a saving of more than £200 per annum, whilst in most breweries of that size the saving would be considerably greater. After having referred to certain improvements in connection with mashing procedure, the author discussed the Meura process, in which a converter and filter press are used in place of the ordinary mash-tun. Owing to the possibility, or rather the necessity, of dealing with finely ground malt, and to the perfect control over the mashing operations which the use of a properly constructed converter gives, the brewer is enabled to obtain from the malt practically the whole of its available extract, whilst the use of a filter press enables the resulting extract to be obtained both rapidly and completely. Having referred to certain improvements in connection with the employment of hops, the author proceeded to discuss the question of cooling as affecting the stability of the beer. It was pointed out that in most cases the advantages of employing a cooler were very much more than counterbalanced by the bacterial infection occurring at this stage, and the author advocated the replacement of the cooler by a deep collecting vessel and refrigeration in a room supplied with purified air. Having referred to the construction of fermenting vessels, and having alluded incidentally to the recent employment of aluminium for that purpose, the author discussed what he described as one of the most striking changes which had taken place in the brewing industry during recent years, namely, the enormous development of the bottle trade. The various chilling and filtration systems were referred to, and the author directed special attention to a recently introduced process, the essential features of which are the charging of the chilled beer with natural fermentation gas, its storage at a low temperature for the deposition of sediment and some maturation, and its filtration and racking in a brilliant condition into cask. It was pointed out that this system is in successful operation in a number of breweries in this country, and that it possesses several important advantages, particularly in the brewing of running mild ales.

The Author concluded by remarking that owing to its tonic and mildly stimulating properties, and to the presence of a not inconsiderable proportion of nutritive constituents in a readily and almost completely assimilable form, beer stood practically alone among beverages, and unquestionably occupied a position among our food stuffs (using this expression in its widest sense) which it was likely long to maintain, and from which it was highly undesirable that it should ever be displaced. The times were, he said, admittedly critical, and never was there a period when there was so great a necessity for maintaining and improving quality, and for taking every possible step to secure the highest manufacturing efficiency. The race would be to the best equipped, and it was only by taking advantage of every improvement in working that science could suggest that brewers would be able to emerge successfully from the period of stress and strain through which the industry was passing.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 1st, 1911.

Mr. E. W. Voelcker, President, in the Chair.

Messrs. Ronald Leslie Collett, William Beaverly-Cowie, Frank Evershed, and George Taylor were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Horace G. Battye, 24, Malvern Road, Berston Hill, Leeds; George Davidson Elsdon, City Analyst's Laboratory, Council House, Birmingham; Norman Evers, Bedcote House, Stourbridge; and Arthur William Knapp, 275, Birchfield Road, Birmingham.

Certificates were read for the second time in favour of Messrs. Joseph Clifford, James Connah, Harley F. Knight, Charles H. La Wall, William Rest Mummery, and W. Macro Seaber.

The following papers were read and discussed :—

"*Examination of Shrewsbury and Knapp's Process for the Ectimation of Cocoanut Oil.*" By Raymond Ross, Joseph Race, and Frank Maudsley.

A number of foreign butters have been examined by this process and the limits of accuracy determined.

The mechanism of the process and its use in analysis of certain fats other than butter are discussed.

"*Estimation of Ferrous Iron by Permanganate in presence of Hydrochloric Acid.*" By Charles Alexander Cumming and Alexander Gemmell.

The error due to hydrochloric acid in this titration is diminished by the addition of salts capable of yielding an unionised or slightly ionised chloride, *e.g.*, mercuric, cadmium, or zinc. Objections are raised to the addition of manganese sulphate, which has been proposed as a remedy for this error. The best results were obtained by the addition of phosphoric acid before titration (without the manganese sulphate used in Reinhardt's solution).

"*Analysis of Sweetened Condensed Milk.*" By Arnold Backe, A. Wiborg, and E. Roer.

Sweetened condensed milk always contains crystals of milk sugar, sometimes sufficiently large "to make the milk gritty to the taste." On standing the cream rises, and the crystals of milk sugar fall; as much as 10 per cent difference between the milk sugar in the top and bottom layers has been observed. It is essential for analysis to mix thoroughly or to dilute with water the whole contents of a tin.

"*Estimation of Petroleum in Turpentine.*" By H. S. Shrewsbury.

The author has tried H. C. Frey's method (*Journ. Am. Chem. Soc.*, 1908, p. 420). 10 cc. of the turpentine are shaken with 30 cc. of aniline for five minutes, and the mixture left to separate. Working at 28° C., prepared mixtures of turpentine and a petroleum (the ordinary pitch oil of Trinidad) gave the following figures:—

First figure of each pair gives per cent by volume petroleum present; second figure, petroleum measured after thirty minutes standing:—0, 0; 1, 0; 5, 0; 10, 0; 30, 30; 50, 54; 70, 70; 90, 80; 95, 84; 99, 84.

"*Notes on the Formation of Hypoiodites and their Action on Sodium Thiosulphate, a Source of Error in certain Iodine Titrations.*" By J. P. Batey.

In titrating a solution of tartar emetic (potassium antimonyl tartrate) by adding excess of iodine and titrating back with sodium thiosulphate in presence of bicarbonate, a high result was obtained. To determine the cause of this a number of experiments have been made, and it has been shown that alkaline hypoiodites oxidise sodium thiosulphate to sulphate (*i.e.*, beyond the tetrathionate stage). From the evidence obtained it would appear that when iodine solution is mixed with sodium bicarbonate some hypoiodite is produced. On titrating the mixture with thiosulphate some of the latter is oxidised to sulphate by the hypoiodite, thus introducing an error.

RÖNTGEN SOCIETY.

A 10,000 *Volt Storage Battery.*

By the invitation of Mr. Alan A. Campbell Swinton the meeting of the Röntgen Society on March 2nd was held at 66, Victoria Street. Mr. Swinton carried out a number of experiments with a 10,000 volt Storage Battery which has been constructed under his supervision, and which, obviously, it would have been difficult to have conveyed to the Society's usual place of meeting. Mr. Swinton said that the construction of this battery was due to a suggestion made by Sir William Crookes at a meeting of the Royal Society. He (Mr. Swinton) had shown on that occasion a number of experiments made upon electrical discharges through high vacua, and Sir William expressed the opinion that it was time an attempt was made to repeat the effects with the continuous current from a battery. A number of large storage batteries had been constructed at various times. One of the most notable was that of De la Rue, which consisted of 11,000 cells. Their utility, however, was strictly limited, and, with the coming of the high-speed electro-static machines, he thought that their days were numbered. His own battery, constructed by two of his assistants, consisted of 4800 cells, contained in five sections, each holding 960, and each of these sections was further divided into 24 blocks of 40 cells each. The battery was charged at a very low rate—not exceeding 10 milliampères, and was capable of discharging at a rate of 150 milliampères or over for several minutes. Short-circuited, it would probably give 2 or 3 ampères, and was certainly a dangerous machine.

Mr. Swinton carried out a number of experiments to show that every one of the effects he had obtained with electrical discharges through high vacua could be repeated with his battery. He reproduced certain electro-capillary effects, and also the phenomena obtained in vacuum tubes owing to the "Canal" rays. All the ordinary effects with a Crookes tube could be repeated. An ample cathode stream was forthcoming, and although, on the occasion of the experiment, there were apparently no X-rays, Mr. Swinton said that it was possible to obtain a very feeble X-ray effect with 10,000 volt continuous current in this manner. The concluding experiment showed the development of striæ in the fluorescence seen in a long horizontal tube when the current was switched on from the battery.

In the course of the discussion which followed, Mr. W. Duddell thought it unlikely that many high-tension batteries would be constructed. Two other alternatives were open. One was the construction of influence machines, which of late years had made considerable progress; the other was the building of a direct current generator. With regard to the striated appearance of the fluorescence in vacuum tubes, Mr. Duddell thought that the striæ represented the points at which ionisation was taking place, the molecules of gas breaking up and forming steps, the distance apart of which depended upon the potential gradiant and the mean free path of the molecules.

Mr. C. E. S. Phillips did not agree that these batteries were quite such useless things as had been suggested. There were still some outstanding problems in electricity, especially with regard to spectrum observation, which might be tackled from the battery point of view.

Mr. Swinton, in reply, said that he attributed the absence of trouble with his battery, in spite of the use of celluloid separators in the cells, to the very low charging current they had used, thereby avoiding the bubbling of acid. When restricted to this low current density in charging, everything was maintained in a dry condition.

NOTICES OF BOOKS.

Dispensing Made Easy. By Wm. G. Sutherland, M.B., Aberd. Fourth Edition. Revised by F. J. Warwick, B.A., M.B. Cantab., M.R.C.S., L.S.A. Bristol: John Wright and Sons, Ltd. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1910.

This little manual is well known as a convenient book of reference for the busy doctor who does his own dispensing. It is thoroughly practical in every respect, and contains many hints and suggestions which make for economy; all the formulæ and prescriptions given have been repeatedly tested, and their relative value is specially pointed out. To make room in the fourth edition for new matter and formulæ some of the original contents have been deleted, but the general plan has not been altered and the book remains one of the handiest for the busy practitioner.

Die Absorption. ("Absorption"). By J. M. van Bemmelen. Edited by Dr. W. Ostwald. Dresden: Theodor Steinkopff. 1910. (12 marks).

Professor Bemmelen's work on colloidal chemistry and absorption is undoubtedly less well known than its value and importance would warrant, and Dr. Ostwald is to be congratulated upon having undertaken the task of editing this collection of his articles. They have been selected and arranged by the author himself, and their perusal will give a very clear idea of the historical development of the subject. A bibliography has been added by Dr. W. P. Jorissen, who, in addition, has contributed a short biography of Professor Bemmelen.

Preparation of Ketene from Acetone. — Julius Schmidlin and Maximilian Bergman. — By leading acetone vapour through a glass tube filled with pieces of clay and heated to 500—600° a yield of 10—14 per cent of ketene can be obtained. Thus the decomposition of acetone takes place in two stages:—I. At 500 — 600°: $2CH_3.CO.CH_3 = 2CH_2{:}CO + 2CH_4$; II. At temperatures above 500–600°: $2CH_2{:}CO = 2CO + C_2H_4$. The ketene gas thus obtained can be used as a convenient gaseous acetylating agent.—*Berichte*, xliii., No. 15.

CORRESPONDENCE.

THE BUNSEN CENTENARY.

To the Editor of the Chemical News.

Sir,—On March 31st it will be one hundred years since Robert William Bunsen was born, and it has been felt that that occasion should not be allowed to pass without his pupils and admirers in this country giving expression to their veneration of the memory of one of the greatest chemists of our times. A Committee has been formed to make the necessary arrangements, and it was intended to celebrate the centenary by a dinner. Unfortunately, the two most distinguished pupils of Bunsen, Sir Henry Roscoe and Sir Edward Thorpe, are at present prevented by indisposition from attending such a celebration. Under these circumstances the Committee has decided not to proceed with the arrangements for a dinner; but, feeling that the occasion should not be allowed to pass unnoticed, they have resolved to send a signed Address to the Heidelberg University from old Heidelberg students in this country, and to place a wreath on the Bunsen monument. May we request those old Heidelberg students who wish to participate in this movement to send their signatures to Prof. H. B. Dixon, of the Manchester University, the chairman of the committee, or to either of the undersigned honorary secretaries.—We are, &c.,

Francis Jones (Manchester Grammar School),
J. Grossmann (Plymouth Grove, Manchester).

Chemical Laboratory,
157, Plymouth Grove, Manchester,
March 11th, 1911

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliı., No. 3, January 16, 1911.

Radiation of Quinine Sulphate, Ionisation and Luminescence.—M. de Broglie and L. Brizard.—Quinine sulphate, after it has been heated, discharges an electroscope, the salt also becomes phosphorescent and undergoes variations in its state of hydration. The radiation emitted by quinine sulphate is very readily absorbed. When crystals are watched in the dark while they are being hydrated a scintillation and a continuous luminosity are observed, both of which appear to be due to small electric discharges produced as the crystals are ruptured. The ionisation of the gas in the neighbourhood of the crystals, the effects of varying pressure, and other phenomena appear to confirm this view.

Brown Gold.—M. Hanriot.—The author has studied quantitatively the contraction which brown gold undergoes on heating, and finds that it reaches a definite value at the end of five or six hours. He has also determined the influence of temperature, mode of heating, composition of the original alloy, &c., on the contraction.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xliii., No. 17, 1910.

Electrolytic Oxidation of Aromatic Sulphides.—Fr. Fichter and Ph. Sjöstedt.—With benzyl sulphide three different products can be obtained by electrolytic oxidation, according to the experimental conditions. If a solution of the sulphide in acetic acid is electrolysed, using a platinum anode, and concentrated hydrochloric acid is added in the cold, a good yield of benzyl-sulphoxide is obtained. If the solution is warmed the chief product is benzyl-disulphoxide, $C_7H_7.S_2O_2.C_7H_7$, while when concentrated sulphuric acid is substituted for hydrochloric acid the hitherto unknown tribenzyl-sulphinium sulphate, $(C_7H_7)_3S.SO_4H$. is obtained.

Mercerised Cellulose.—O. Miller.—It has been supposed that mercerised cotton is a hydrated cellulose, but when cellulose is mercerised no increase of weight occurs, and Gladstone proved that mercerised and ordinary cellulose have the same composition. They are not, however identical, for the former has the power of adsorbing a greater amount of moisture than the latter, and retaining it more persistently. The change which occurs on mercerisation is probably of the nature of an isomerisation. The degree of mercerisation can be determined by substantive dyes.

Determination of Quinone by means of Titanium Chloride.—Edmund Knecht and Eva Hibbert.—Quinone is quantitatively reduced by $TiCl_3$ in the cold, according to the equation $C_6H_4O_2+2HI=C_6H_6O_2+I_2$. The estimation can be carried out by dissolving the quinone in hot water, adding excess of $TiCl_3$ solution, and then determining the excess by iron alum, using potassium rhodanide as an indicator. Or the titration can be performed directly, a trace of methylene blue being used as indicator. The quinone is quantitatively reduced before the reduction and decolorisation of methylene blue begins.

Zeitschrift für Anorganische Chemie. Vol. lxix., No. 3, 1911.

A very Basic Violet Chromic Acetate. — Ernst Gussmann.—By adding pyridine to a solution of the biacetate of the hexacetatotrichromic base and heating to boiling for half a day the grey-green acetate of the hexacetatotripyridine-trichromic base is obtained, while from the violet mother-liquor the violet acetate of formula $Cr_2(OH)_3(CH_3COO)_3.9H_2O$ crystallises out. This basic acetate is very difficultly soluble in hot and cold water. It gives a violet solution with phenol. The molecular weight of the compound corresponds to the simple formula.

Double Nitrates of the Rare Earths.—G. Jantsch and S. Wigdorow.—According to the author's experiments the double nitrates of sodium, potassium, and cæsium have the following formulæ: — $[La(WO_3)_5]Na_2.H_2O$, $[La(NO_3)_5]K_2.2H_2O$, $[La(NO_3)_5Cs_2.2H_2O$, and $[Ce(NO_3)_5]Na_2.H_2O$. The rubidium and thallium double nitrates fuse in their water of crystallisation fairly sharply at a definite temperature. This melting-point, as the following table shows, falls as the atomic weight of the rare earth metal increases :—

$[La(NO_3)_5]Rb_2.4H_2O$	86°
$[Ce(NO_3)_5]Rb_2.4H_2O$	70
$[Pr(NO_3)_5]Rb_2.4H_2O$	63·5
$[Nd(NO_3)_5]Rb_2.4H_2O$	47
$[La(NO_3)_5]Tl_24H_2O$	72
$[Ce(NO_3)_5]Tl_2.4H_2O$	64·5

The authors have found the molecular volumes of the double nitrates to be as follows :—

$[La(NO_3)_5]Na_2.H_2O$	195·08
$[Ce(NO_3)_5]Na_2.H_2O$	194·00
$[La(NO_3)_5]K_2.2H_2O$	221·76
$[La(NO_3)_5]Cs_2.2H_2O$	265·5
$[La(NO_3)_5]Rb_2.4H_2O$	277·1
$[La(NO_3)_5]Tl_2.4H_2O$	280·0
$[Ce(NO_3)_5]Rb_2.4H_2O$	277·6
$[Ce(NO_3)_5][Tl_2.4H_2O$	279·7
$[Pr(NO_3)_5]Rb_2.4H_2O$	277·4
$[Nd(NO_3)_5]Rb_2.4H_2O$	272·3

Besides the lanthanum rubidium nitrate of formula $La(NO_3)_5[Rb_2.4H_2O$ they have prepared an acid salt, $[La(NO_3)_4]Rb.HNO_3$.

Proportion of Cl, SO_3, and σ_0 Values in Sea-water.—Ernst Ruppin.—In this paper the author gives tabulated results of the determinations of Cl, SO_3, and the σ_0 values of fourteen different specimens of sea-water tested in the hydrographic laboratories at Kristiania, Helsingfors, Kiel, Monaco, and Nancy.

Metatungstic Acid.—Arthur Rosenheim and Franz Kohn.—Metatungstic acid is an aquo compound and is thus to be classed not as an isopoly acid but as a heteropoly acid. The complex anion probably contains three molecules of water, and its formula is—

$$H_2\left[WO\begin{matrix}(WO_4)_3\\(H_2O)_3\end{matrix}\right] + Aq.$$

The pure acid is insoluble in ether. In water it behaves like a normal electrolyte, and reacts like a dibasic acid. In absolute alcoholic solution, on the other hand, it exhibits the properties of a colloidal substance. Esters of the acid cannot be prepared. The results obtained do not agree with the assumption of Coplaux, that metatungstic acid is $H_{12}W_{24}O_{78}.3H_2O + Aq$.

Telluric Acid Oxalates.—Arthur Rosenheim and M. Weinheber.—If telluric acid is added to an aqueous solution of an alkali oxalate, telluric acid oxalates crystallise out; thus the potassium, rubidium, and cæsium salts have been prepared. The authors have determined the solubility of the salts in water at different temperatures. If the solubility of the potassium salt is compared with that of potassium tellurate and of oxalic acid it is found that the solubility shows a very decided decrease, which is a proof of the formation of a complex.

Gravimetric Determination of Tellurium and Alkalimetric Determination of Telluric Acid. — Arthur Rosenheim and M. Weinheber.—To determine tellurium gravimetrically the aqueous solution of a tellurium compound is treated with a faintly ammoniacal solution of hydrazine sulphate and heated to 130° in a low pressure autoclave. The tellurium then separates in a glittering grey deposit, and may be filtered off and dried in an atmosphere of CO_2. Telluric acid forms with glycerin a glycerin telluric acid. If a large excess of barium hydroxide solution, or barium chloride and caustic soda, is added to a telluric acid solution, $BaTeO_4$ is precipitated, and can be filtered off and the excess of alkali titrated with oxalic acid.

Preparation of Phenylnitromethane. — Panchánan Neogi and Birendra Bhusan Adhicary.—A good yield of phenylnitromethane can be obtained by heating dry mercurous nitrite with benzyl chloride on a water-bath, distilling *in vacuo*, and then again fractionating the liquid.

Thermochemistry of Silicates.—Emil Dittler.—The heating and cooling curves of silicates cannot be determined accurately owing to the difficulty of ascertaining the rate at which to heat, and it is found that the melting-points are higher the larger the crystals of which the mass consists. It depends upon the method whether the transformation to the amorphous state is sharp and easily detected when the ultramicroscope is used.

MISCELLANEOUS.

Chemical Laboratory Fresenius, Wiesbaden, Germany.—At the Autumn Vacations Course, 1910, held at the Laboratory Fresenius, 33 students took part. During the regular Winter Term, 1910-11, 36 students were inscribed, including 6 ladies. The nationality of the students was as follows:—24 were from Germany, 3 from Russia, 2 from France, 1 from England, 1 from Austria, 1 from Holland, 1 from Italy, 1 from Spain, 1 from Turkey, and 1 from Brazil. The Directors of the Institute, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, are assisted by four duly qualified lecturers and heads of departments. Besides these there is a staff of 21 assistant chemists and 9 sub-assistants, including 5 ladies. The next Summer Term will commence on April 24th, 1911. During the Winter, 1910-11, a number of scientific treatises originated from the Laboratory Fresenius; they were published in different chemical journals, especially in the *Zeitschrift fur Analytische Chemie*, edited by the Directors. As special print appeared "Chemische und Physikalisch-chemische Untersuchung der König Ludwig-Quelle zu Fürth bei Nürnberg, sowie Untersuchung derselben auf Radioaktivität," by Geh. Regierungsrat Prof. Dr. H. Fresenius, Wiesdaden, C. W. Kreidel's "Verlag." Besides the scientific work, a great number of chemical analyses were executed during the Winter half year, 1910-11, for commercial, mining, industrial, and agricultural purposes, also in the interest of sanitary boards, criminal, and other States departments.

American Society of Mechanical Engineers.—The Sixty-third Meeting of the Society will be held in Pittsburgh, Pa., from May 30th to June 2nd, inclusive. The Society has not met in this city since 1884. The Society is one of the foremost organisations of technical and professional engineers in the world, with a membership of over 4000 in this country as well as abroad. The headquarters of the Society are in New York City, and Col. E. D. Meier, of St. Louis, is President this year. The Society has in the Pittsburgh district alone a membership of about 160. Last year the Society held a joint meeting in England with the British society, the Institution of Mechanical Engineers. George Westinghouse, who was President of the Society last year, presented a paper on the "Electrification of Railroads," which aroused a great deal of interest. The British society through its local committees in Birmingham and London entertained the American engineers by showing them many things of professional interest, as well as providing delightful social functions. An Executive Committee, consisting of E. M. Herr, Chairman, George Mesta, J. M. Tate, jun., Chester B. Albree, D. F. Crawford, Morris Knowles, and Elmer K. Hiles, Secretary, will have charge of the Pittsburgh meetings. It is expected that from 300 to 400 members and ladies will be in attendance. There will be professional sessions when papers will be read and discussed. There will also be inspection trips through the leading local industrial establishments, besides automobile trips through the parks, a visit to Carnegie Institute, Memorial Hall, &c.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Royal Society of Arts, 8. "Applications of Electric Heating," by Prof. J. A. Fleming, F.R.S.

TUESDAY, 21st.—Royal Institution, 3. "Explorations of Ancient Desert Sites in Central Asia," by M. Aurel Stein.

WEDNESDAY, 22nd.—Royal Society of Arts, 8. "Manufacture of Portland Cement," by A. C. Davis, Assoc.Inst.C.E.

THURSDAY, 23rd.—Royal Institution, 3. "Giants and Pygmies," by Prof. Arthur Keith, M.D.

—— Royal Society. "A Theory of Asymptotic Series," by G. N. Watson. "Ionisation of Heavy Gases by X-rays," by R. T. Beatty. "Variation of the Ionisation with Velocity for the β-Particles," by W. Wilson. "Causes of Absorption of Oxygen by the Lungs in Man," by C. G. Douglas and J. S. Haldane. "Influence of Planets on the Formation of Sun-spots," by Dr. A. Schuster.

FRIDAY 24th.—Royal Institution, 9. "The Sidereal Universe," by Sir David Gill, K.C.B., &c.

—— Physical, 5. At the City and Guilds (Engineering) College "A Sensitive Thermo-regulator" and "Experiments on the Measurement of Electrolytic Resistances using Alternating Currents," by H. F. Haworth. "Oscillatory Currents in Coupled Circuits" and "Some Radio-telegraphic Apparatus in Use at the City and Guilds (Engineering) College," by G. W. O. Howe.

SATURDAY, 25th.—Royal Institution, 3. "Radiant Energy and Matter," by Prof. Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. CIII., No. 2678.

STUDIES OF THE PROCESSES OPERATIVE IN SOLUTIONS.

XVI.—The Relative Efficiencies of Acids as Deduced from their Conductivities and Hydrolytic Activities (II).

By HENRY E. ARMSTRONG and EDWARD WHEELER.

In our previous communication under this title, a series of observations made with chlorhydric, nitric and sulphuric acids was described which indicate that these acids are of equal hydrolytic activity in solutions of the following concentration :

$HNO_3(55{\cdot}5H_2O)$ $HCl(3+55{\cdot}5H_2O)$ $H_2SO_4(7+55{\cdot}5H_2O)$

The relative molecular conductivities of such solutions are represented by the ratios :

100 101·5 121.

On the other hand, the hydrolytic activity of solutions which are equal in molecular conductivity is expressed by the ratios :

$HNO_3 : HCl : H_2SO_4$ 100 : 107 : 180.

Taken in conjunction with the fact that hydrolytic activity and molecular conductivity are influenced in opposite directions by changes of concentration, such results afford clear proof that chemical activity and electrical conductivity cannot be conditioned by the same or even by similar operations.

Preliminary experiments were referred to which appeared to indicate that in very concentrated solutions the apparent molecular conductivity of hydrogen chloride is lower than that of hydric nitrate in solutions of equivalent strength—in other words, that a change takes place in the sign of the difference between the two acid solutions as the concentration is increased. This surmise has now been verified.

Our later results are summarised in Tables I and II. It will be noticed that whilst the apparent hydrolytic activity of chlorhydric acid increases as the concentration is raised and far more rapidly than in the case of nitric acid, molecular conductivity diminishes until the small positive difference in favour of chlorhydric acid when 50 molecular proportions of water are present becomes a similar negative difference when the concentration is raised to between 30 and 40 molecular proportions of water ; this difference continues to increase as the concentration is increased. As hydrogen chloride is on the point of escaping rom the most concentrated solutions examined, it may be supposed that the rapid fall in conductivity is due to the change in the state of the solution which takes place as the saturation point is approached.

Table I.

Hydrolytic activities at 25°, using acid and water in the molecular proportion 1 acid : x water, sugar being present in the molecular proportion 1 : 55·5 molecules of water :

			k at x'.		K.	
x	y	x'	HCl	HNO_3	HCl	HNO_3.
18	3·08	17·88	3454	2704	1120	877
20	2·78	19·86	2847	2243	1026	808
25	2·22	24·84	1796	1551	809	699
30	1·85	29·80	1311	1124	709	608

In this table y is the molecular proportion of acid present in 1000 grms. of water.

x' is the amount of water in gram-molecular proportions present when three-quarters of the change has taken place.

It is necessary to determine the activity at a known concentration, as in concentrated solutions the value changes very rapidly.

$K = k/y$ is the assumed hydrolytic activity per molecular proportion of acid.

Table II.

Molecular conductivities (μ) in solutions containing 1 gram-molecular proportion of acid and x gram-molecular proportions of water at 25°.

x	HCl	HNO_3	Difference.
10	169·03	178·90	−9·9
15	221·19	227·57	− 6·4
18	242·35	248·01	− 5·6
20	254·05	258·18	− 4·1
25	276·67	279·67	−3·0
30	292·75	294·89	−2·1
40	314·38	314·64	−0·3
50	328·44	327·35	+1·1
60	337·97	335·31	+2·6

It may fairly be assumed that hydrogen chloride enters into solution entirely in the form of simple unitary molecules. Whatever changes attend its dissolution, whatever the composition of the acid that is formed by the interaction of the halogen hydride and water, however complex the solution may be that is produced because of the variety of compounds present, the changes to be considered are those involved in the interaction of molecules represented by the simple formula HCl and the various molecules—some simple, some complex—present in water.

This argument does not apply to hydric nitrate and hydric sulphate, as these are not only more or less "associated" in the liquid state but presumably also present in solution to some extent in this condition ; the changes which attend dissolution must, on this account, be more complex in the case of the oxygenated compounds than in that of the halogen hydride.

The problem presented by solutions of hydrogen chloride is therefore the simplest possible, as the dissociation of molecular complexes of the solute has not to be taken into account and the only changes to be considered are those occurring in the solvent and between solvent and solute.

Only two compounds capable of giving rise to composite electrolytes are known which are comparable with hydrogen chloride in molecular simplicity and equally free from the taint of association—the halide hydrides, hydrogen bromide and hydrogen iodide.

We have therefore deemed it desirable to institute a comparison between the three acid solutions formed from the three hydrides. Their hydrolytic activities are recorded in the following table :

Table III.

Hydrolytic activities at 25° of equivalent solutions containing 1 gram-molecular proportion of halogen hydride and x gram-molecular proportions of water.

x	HCl	HBr	HI
40	806	944	—
50	580	659	751
60	448	499	567
80	303	333	365
100	228	247	—

Molecular conductivities at 25° of equivalent solutions containing 1 gram-molecular proportion of halogen hydride and x gram-molecular proportions of water.

x	HCl	HBr	HI
25	277	281	—
30	292	298	—
40	314	320	324
50	328	—	335
55·5	335	339	342
60	338	345	346

Obviously, bromhydric acid is only slightly stronger than chlorhydric acid and iodhydric acid only slightly stronger

than bromhydric acid, judging from their molecular conductivities; they differ to a far greater extent in hydrolytic activity.

The results recorded in table IV show that the haloids differ in a corresponding manner in the influence they exercise.

TABLE IV.

Hydrolytic activities (K) of bromhydric and iodhydric acids in presence of 1 gram-molecular proportion of the corresponding haloid in solutions containing x gram-molecular proportions of water.

	$x = 50$	60	80	100.
KBr	962	699	438	308·5
KI	1194	839	505	—
NaBr ..	1032	749	453	324
NaI	1312	897	522	—
NH_4Br ..	943	678	431	303

These results are proof that the activity of the haloid varies in the same direction as that of the halide varies, the iodide having a greater influence than the corresponding bromide, the bromide a greater influence than the chloride. A better idea of the character of the relationship is given on contrasting the apparent hydration values of the halogen halides and of the corresponding haloids deduced in the manner described in the communication by F. P. Worley (table V).

TABLE V.

Apparent Hydration Values of the Halogen Hydrides and Haloids at Different Concentrations.

		$x = 40$	50	60	80	100
I.	HCl	13·6	15·1	16·8	18·7	19·8
	HBr	16·2	17·6	18·7	21·5	24·3
	HI		19 to 20	23 to 24*		
II.	NaCl ..		—	12·3	14·0	15·6
	NaBr ..	—	14·5	13·6	16·8	21·8
	NaI	—	15·5	16·3	—	—
III.	KCl		10			
	KBr	—	10·6	11·8	14·4	17·8
	KI	—	13·1	13·6	—	—
IV.	NH_4Cl ..		10			
	NH_4Br ..	—	9·9	11·2	13·3	16·2

* It is impossible to deduce more than approximate values on account of the flatness of the curves. The values given were determined at concentrations between those studied in the case of the chloride and bromide.

These values are of significance in a variety of ways. In the first place, it is to be noted that those entered in section I represent the apparent hydration values of the acid-sugar-water systems, whilst those entered in sections II—IV are differences between the values of these systems and those obtained when the salt is present; the latter may therefore be regarded as the apparent hydration values of the haloids.

The hydrides of the halogen elements are to be regarded as less active substances than the metallic halides (the haloids), in the sense that they display less residual affinity —in other words, the halogen atom is less exhausted by combination with the metal than it is by combination with hydrogen. This follows from the fact that whilst the hydrides are all gaseous substances, the metallic derivatives are solids boiling at very high temperatures; apparently the only interpretation of this difference which is open to us is that the molecules of the metallic compounds are complex substances of the order $(NaCl)_x$, $(NaBr)_y$, $(NaI)_z$, x, y and z being factors of unknown value.

From the point of view urged above, it is to be supposed that the halogen hydrides are present in solution as simple molecules—as HCl, HBr, HI—associated in various ways with molecules of hydrone (OH_2). The values given in section I (table V) are therefore in a sense maximum values —they express the maximum extent to which "water" is associated with and influenced by halogen hydrides. The values given in the remaining sections cannot be interpreted so simply; if the metallic halides were present in solution only as simple molecules, their influence should be greater—perhaps to a very considerable extent—than that of the halogen hydrides; the fact that the apparent hydration values of the metallic halides fall so considerably below those of the halogen hydrides cannot well be interpreted otherwise therefore than as evidence that the complex molecules of the haloid are only partly dissociated in solution.

It is very difficult to carry the analysis beyond this stage. In any case, it would appear to be impossible to give an absolute interpretation of the behaviour of such solutions: they can only be regarded as regions in which equilibrium is dependent on the occurrence of a variety of changes.

To render the dissociation of the haloid complex complete, dilution must be carried very far, as molecular conductivity approaches to a maximum only when the solution is very highly diluted in the case of the haloids—whilst in the case of the halogen hydrides a moderate degree of dilution suffices to raise the molecular conductivity almost to its maximum value.

Similar considerations are applicable in explanation of the differences in molecular conductivity observed in the case of chlorides, bromides and iodides at different degrees of dilution. For example:

Molecular Conductivities at 25°.

	In weight-normal molecular solutions.			At practically infinite dilution.		
	Cl	Br	I	Cl	Br	I
H ..	335·3	339·6	342·1	403	405	406
K ..	112·3	116·3	118·5	148	150	150
Na ..	85·9	90·2	92·5	126	127	128

In point of fact, we have no measure of the proportion of electrolytically active molecules present in the solutions; it cannot well be assumed that more than a certain proportion of molecules become activated; the similarity in the values, under corresponding conditions, in the case of compounds of the three halogens, cannot even be regarded as proof that the solutions contain equal numbers of active molecules, as the activities may well be different and the proportion of active molecules different in a corresponding degree—the marked difference in the behaviour of the three halogens in their organic derivatives being an argument of weight in favour of this view. It is by no means impossible or even improbable that chloride, bromide and iodide tend to form hydrated compounds of different types or that this or that type of hydrate is more stable in the case of the one than in that of the other. The advocates of the ionic dissociation hypothesis have left all such chemical considerations out of account; it were time that chemists considered the problem in its chemical aspects.

Whilst engaged with hydrogen bromide and iodide, we have deemed it desirable also to determine the changes in volume which attend the neutralisation of bromhydric and iodhydric acids by potassium and sodium hydroxides (compare Part VI) The values deduced are as follows:

Volume of weight-normal solutions at 25°.

KOH	1014·68	HBr	1028·43
NaOH ..	1001·28	HI	1039·88

Water: 1000 grams = 1002·97 c.c.; 18 grams = 18·05 c.c.

KOH + HBr = 2943·11 − 2005·94 = 37·17 c.c.
KBr = 1038·54 + 18·05 − 1056·59 − 1002·97 = 53·62 c.c.
Expansion = 16·45 c.c.

NaOH + HBr = 2029·71 − 2005·94 = 23·75 c.c.
NaBr 1028·33 + 18·05 = 1046·38 − 1002·97 = 43·41 c.c.
Expansion = 19·66 c.c.

KOH + HI = 2054·56 − 2005·94 = 48·62 c.c.
KI 1049·78 + 18·05 = 1067·83 − 1002·97 = 64·86 c.c.
Expansion = 16·24 c.c.

$NaOH + HI = 2041{\cdot}16 - 2005{\cdot}94 = 35{\cdot}22$ c.c.
$NaI = 1039{\cdot}28 + 18{\cdot}05 = 1057{\cdot}33 - 1002{\cdot}97 = 54{\cdot}36$ c.c.
Expansion = 19·14 c.c.

In the following table, our values of the expansions in weight-normal molecular solutions are compared with those given by Ostwald as observed in solutions containing equivalent proportions of the solute per kilogram : *

Table VI.

	A and W.		Ostwald.	
KNO_3	16·57	3·14	20·05	0·28
$NaNO_3$ ..	19·71		19·77	
KCl	16·28	3·09	19·52	0·28
NaCl	19·37		19·24	
KBr	16·45	3·19	19·63	0·29
NaBr	19·66		19·34	
KI	16·24	2·90	19·80	0·26
NaI	19·14		19·54	

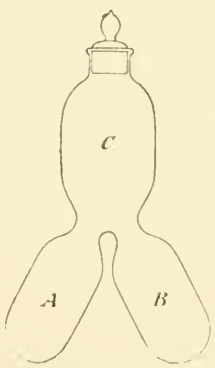
The values differ but slightly in the case of corresponding chloride, bromide and iodide—so slightly as to be within the limits of experimental error. It is possible that if average values were deduced from a considerable number of experiments, they would be in the order observed in the case of hydrolytic activity and molecular conductivity but this by no means follows. As in all cases the change undergone by the alkali is the same, it is to be supposed that it contributes in a constant manner to the expansion, whatever acid be used ; each acid, however, will contribute its own proper share of hydrone and cause expansion accordingly ; the stronger acid would probably yield up more hydrone but if the salt formed from it were also "stronger" than that of the weaker acid, it would cause greater contraction by associating with more hydrone. Such cross effects might either balance each other or even give rise to negative variations. The change observed must depend on the manner in which "hydration" is effected—especially on the extent to which "hydrolates" and "hydronates" are formed ; it is to be expected that the production of the former would involve greater alteration in volume than that of the latter, as hydronates are probably more nearly related in structure to the polyhydrones which are presumably the dominant components of water and as the volume does not increase to any marked extent, although more "water" becomes associated with the haloid (compare Part VI, p. 86).

Little need be said as to the manner in which the experiments were made. The hydrogen chloride was prepared from purified sulphuric acid and fused purified salt ; the chlorhydric acid was made by passing hydrogen chloride into water and standardised by weighing the silver chloride precipitated from a known weight of the liquid. The bromhydric and iodhydric acids used were purchased materials ; the solutions were standardised gravimetrically. In the case of iodhydric acid, the colour due to iodine was removed by means of sulphurous acid before standardising the solution ; in the actual experiments, the decoloration was effected just before using the acid by passing a few bubbles of hydrogen sulphide into the solution and then filtering it quickly through ashless filter paper.

It was impossible to prevent oxidation from taking place during the period of hydrolysis ; by leaving hydrogen sulphide in the solution, however, the influence of iodine was overcome but the solution gradually became more or less turbid owing to the separation of sulphur. The difficulty thus introduced was partly remedied by increasing the half shadow angle of the polarimeter but the effect of this change was necessarily to reduce the accuracy of the readings.

The haloids used were purified by recrystallisation until neutral ; the less hygroscopic were dried and the required amounts weighed out ; in the case of ammonium bromide —which becomes acid when dried—and sodium iodide, solutions were prepared of approximate strengths and these were standardised. In purifying nitric acid, we availed ourselves of Veley's experience (*Phil. Trans.*, 1898, cxci., 265).

The form of mixing vessel used in preparing the acid-sugar solutions is shown in the figure. The sugar, having been weighed in bulb *A*, was dissolved in water, warming, if necessary ; when the apparatus was cold, it was weighed in order to ascertain the amount of water used in dissolving the sugar. The required amount of acid was then introduced into *B* and the apparatus again weighed ; finally the amount of water required to make up the



solution to the desired strength was introduced and the apparatus weighed once more. The vessel was then placed in a bath maintained at 25°. The warmed solutions were subsequently mixed in *C* and at once transferred to the polarimeter tube, which had been heated at 25°. Readings could be taken within about ten minutes after mixing the solutions ; this was essential, as in the case of the strong solutions the greater part of the change is often over within an hour.

In carrying out the observations, we were able to avail ourselves of the improvements in the instrumental appliances effected by Messrs. Glover and Worley. It will be obvious that the same approach to accuracy cannot be claimed for observations made with concentrated acids, especially with iodhydric, as for those made with the dilute solutions.

* It is clear that our results are in general agreement with Ostwald's but there is a striking difference apparent in that Ostwald's values for the potassium and sodium haloids are practically identical, whilst ours differ considerably ; the difference is due to the difference in concentration. Our solutions were made nominally of equivalent strength, whilst Ostwald used less than the equivalent amount of water in the case of the potassium salts, as he did not take the influence of molecular weight in displacing water into account. Even in our case, however, the solutions were not actually of equivalent strength, assuming that potassium and sodium salts are hydrated to different extents in solution. Strictly speaking, the comparison should be made between solutions containing equal amounts of free water. It would seem that the alteration in volume on neutralisation cannot be taken as a strict measure of the "strength" of an acid or base and that the method is only of value as a means of arriving at approximate values. Apparently, sodium hydroxide is a stronger base than potassium hydroxide ; as this conclusion is scarcely in accordance with current opinion, it is proposed to extend the inquiry to the determination of their relative activities under comparable conditions and to study other hydroxides from a similar point of view.

Infra-red Photographs.—Dr. C. E. Kenneth Mees, who edits the photographic column in *Knowledge*, has been taking some photographs with infra-red rays of light, after the manner recently suggested by Prof. R. W. Wood. Two views obtained in Portugal are given as illustrations. These are chiefly remarkable for the intense blackness of the blue sky, against which the faintest trace of cloud stands out, and Dr. Mees thinks it possible that such photographs might prove of considerable use to meteorologists.

RECENT ADVANCES AND PROBLEMS IN CHEMISTRY.*

By Prof. EMIL FISCHER, Professor at Berlin University.

(Concluded from p. 125).

Through such substances as albuminoids, carbohydrates, fats, &c., chemistry is intimately connected with biology, for the whole of the metabolism occurring in the living organism is a consequence of chemical transpositions taking place among these substances. Hence chemistry is called in to solve the great problems of life, alimentation, growth, fertilisation, heredity, decay, and the many illnesses of the normal state. It is not to be wondered at that in this interesting region keen activity reigns, and we may expect that in the new Institute special attention will be paid to the biological side of our science.

The large institute for the study of fermentation shows how fruitful the collaboration of biologists and chemists may be practically, for in it the results of scientific investigation are at once adapted for the practical needs of brewers and distillers. The Institute has sent a contribution to this evening's little exhibition in the form of a series of beautiful fungus cultures and yeast preparations.

Moreover, chemical and many other industries have profited greatly by organic chemistry. Examples may be drawn from recent times to show this.

Among the carbohydrates cellulose (cell substance) is distinguished by its abundant occurrence in the plant world. It forms cotton and linen, and is the chief constituent of wood, as well as of all the other solid parts of plants. And, now-a-days, what is not made of cellulose? Paper, collodion, celluloid, photographic films, smokeless powder, artificial silk, artificial hair, artificial leather.

Paper is no curiosity in our age of paper, nor celluloid, nor collodion. I did not bring with me smokeless powder or the many other explosives of organic chemistry, because they do not seem to me to be suited for a peaceful lecture theatre. But you see here many beautiful specimens of artificial silk, horse hair, and films which come from the works of Prince G. von Donnersmarck. And in order not to forget competition I have also here to show you photographic films from the Aniline Factory in Berlin, which unlike the ordinary kinds burn with very great difficulty. All these products have been prepared by the skilful combination of chemical and mechanical processes. In order to avoid misconception I must also point out that artificial silk and hair, in spite of their external great resemblance to the natural articles, have a totally different composition, for the natural product does not consist of cellulose, but belongs to the class of albuminous substances.

The beautiful colours which excite our admiration in the artificial textiles also owe their origin to the art of the chemist. They belong to the synthetic coal-tar dyes. This category is so large that at the High Schools lectures extending over a session are delivered upon it. Hundreds of such colours are to be bought commercially, and the value of the substances produced in Germany amounts roughly to 300 million marks. The greater part of them goes abroad.

I must call special attention to synthetic indigo, for it was made after many attempts which were finally attended by complete success. This beautiful crystalline preparation was obtained by sublimation and came from the Badische Anilin und Soda-Fabrik. It is also made at the dye-works at Höchst-a.-M.

The synthetic product is not only much purer and more beautiful, but is also much cheaper than the natural dye. Hence the cultivation of the indigo plant in India has already shrunk to a sixth of its former magnitude, and will probably soon die out altogether. Even the Asiatics colour their wool and cotton with German indigo, of which 38 million marks' worth was exported in 1909.

This is also the place to call attention to the two most important dyes of the living world—chlorophyll and the colouring matter of the blood. The former plays an important part in the fundamental chemical processes upon which the existence of the whole living world depends. I mean the conversion of the carbon dioxide of the atmosphere into sugar, which occurs under the influence of sunlight in the green leaves of plants.

In our own bodies the red colouring matter of the blood has the important task of transporting the oxygen from the lungs to the tissues, and so rendering possible the combustion process which is the source of our bodily and mental power.

I can show you two pure specimens of chlorophyll, one of which is crystalline, I owe these rare preparations to Professor R. Willstätter, of Zürich, who for the last few years has been studying the colouring matter with very fruitful results. The colouring matter of the blood has also been thoroughly investigated recently in Stuttgart and Münich. In these experiments the remarkable result has been obtained that chlorophyll and the colouring matter of the blood are closely allied chemically. This indicates a kind of blood relationship between the plant and animal kingdoms. It must, however, be of great antiquity, *i.e.*, it must go back to the time when there was no distinction between the two kingdoms.

The economic importance of caoutchouc is even greater than that of the coal-tar colours. Its use is continually increasing, and is now estimated at 70,000 tons a year. If the average price of the kilogramme is taken as ten marks this corresponds to 700 millions. It is, therefore, easily understood that the attention of synthetic chemists was attracted to the subject, and nine months ago we heard of attempts to prepare it artificially. As a matter of fact, in August, 1909, the chemists of the Elberfeld Dyeworks, Dr. F. Hofmann and Dr. C. Coutelle, succeeded in finding a practicable method. They used as the initial material the so-called isoprene, a mobile liquid like benzene, which can be prepared synthetically from still simpler materials. By simply heating this liquid in closed vessels it is converted into caoutchouc. I have here a closed glass tube which was originally filled with the mobile liquid isoprene; now after being heated it contains a kind of jelly which is synthetic caoutchouc. When prepared in greater quantity, as this other preparation shows, it is somewhat thicker and pale yellow coloured. The fact that it actually is caoutchouc has been proved by Professor Harries, of Kiel, who has had extensive experience in the scientific investigation of caoutchouc; he has also discovered independently another method for the same purpose.

If synthesis has opened up such a region, it is not limited only to products occurring in nature but by it many other similar substances may be produced. You will therefore not be surprised if I show you other kinds of caoutchoue which have not been obtained from isoprene but from similar liquids, *e.g.*, dimethylbutadiene. We call such products homologues. They have properties very similar to those of caoutchouc, but their chemical composition is different. We cannot yet say which of these different synthetic products is best suited for practical uses. The same may be said of the much more important question of price. But if we think of the fate of natural indigo, of madder dyes, and of similar natural substances we cannot help hoping that synthetic caoutchouc will finally be able to compete successfully with the natural product.

Camphor belongs to the same group as caoutchouc. It also is now made artificially on a large scale. The Aktien Chemical Factory (formerly Schering) of this place led the way in its manufacture. But other firms now prepare it, and the Japanese Government's monopoly of camphor which they acquired owing to the conquest of the island of Formosa is broken down.

I have here another curiosity—artificial resin, which is very similar to amber in external properties, and can be

* A Lecture, illustrated by experiments, delivered in the presence of His Majesty the Kaiser on the occasion of the founding of the Kaiser-Wilhelm Society for the Advancement of Science, on January 11, 1911, at Berlin.

used as a substitute for it, as these chains, combs, cigar-holders, &c., show. These objects have been placed at my disposal by the Bakelite Company of this city. The resin is called bakelite. It is obtained from constituents of coal-tar by a process the principle of which has been known for a long time. But it has been technically perfected, and the preparation made practically useful by the American chemist Baekeland.

In close connection with medicine synthetic chemistry takes an active part in the discovery of new remedies. I can make only a very small selection from the great abundance of its material.

In this flask you see a white powder, a narcotic already much used and called veronal. It has nothing to do with the narcotics of the plant kingdom, opium, &c. It is rather a purely synthetic product. The tenth part of this quantity would be enough to send the whole audience peacefully to sleep. But if the mere sight of the substance in conjunction with the lecture should produce such an effect upon some of my hearers there would be no better antidote than a cup of tea, such as you have in prospect, for tea contains a chemical substance which stimulates the nervous system and the action of the heart. It is also contained in coffee, and was discovered ninety years age by Runge, in this country. The humorous discoverer gave it the name "Kaffeebase," which was afterwards changed to the more euphonious caffeine. It is a curious coincidence that the synthesis of caffeine was also effected here in the University Institute fifteen years ago. From it a method of manufacture was evolved. The contents of this flask are synthetic caffeine prepared by the firm of C. F. Böhringer and Sons, of Mannheim. It is prepared on the large scale from a constituent of guano, uric acid ; but it undergoes such a fundamental chemical change and purification process that it no longer possesses any of the unpleasant properties of the raw material. The chemist can therefore use the same phrase concerning this substance as the Emperor Vespasian used of the gold which was brought to him as a tax from an unsavoury source, *Non olet* (it has no smell).

Pure caffeine is as yet used only as a medicine though in very considerable quantity. It has, however, a much greater importance as the vital principle of coffee, tea, kola nut, Paraguay tea. Hence, after alcohol, it is the most widely used luxury. As soon as it becomes possible to prepare synthetically the aroma of coffee and tea—and this lies within the bounds of possibility—there will be nothing to hinder the artificial preparation of these beverages. And if, on the fiftieth anniversary of the foundation of the Kaiser Wilhelm Gessellschaft, the Principal again issues invitations to tea it is to be hoped that it will be to partake of the synthetic product.

Organic synthesis is not limited to the substances of the plant kingdom, but it attacks with equal intrepidity the products of the animal body.

An instructive example of this is afforded by a remarkable substance (adrenalin), which in our own bodies is secreted by the suprarenal capsules, and plays an important part in the regulation of the blood pressure. Soon after it had been separated in the pure state from the supra renals, Dr. F. Stolz, the chemist of the Höchst Dyeworks, succeeded in preparing it artificially from the constituents of coal-tar. The synthetic product is now put on the market hy the Höchst Dyeworks under the name "Suprarenin." Its very dilute aqueous solution produces a strong contraction of the blood vessels, and hence empties the tissues of the blood. Thus, if we daub a little of this liquid on a skin surface which contains much blood, a red nose for example, it becomes pale in a few minutes. Unfortunately the pallor is not uniform owing to differences in the penetrability of the epidermis. As the action of the substance ceases after some time, and then the original red returns, it cannot be used as a cosmetic, nevertheless it is very useful in surgery. Many operations can be performed without bleeding with the help of this material. This is very convenient for operations on the eye, the roof of the mouth, and the nose.

The Dyeworks at Höchst, which sent me the preparation in many forms, as you will see it here, have also provided different specimens of the new arsenical remedy "Ehrlich-Hata." It is now called "Salvarsan." Anyone who wishes to know more of it can hear of it from an authority, for the discoverer, Professor Ehrlich, is staying among us.

Moreover, the loveliest children of Flora, the sweet-smelling blossoms, have been forced into competition with synthesis. The perfume industry has thus received a great impetus, and in Germany alone products worth from forty to forty-five million marks are produced. I can show you only a few specimens of the many products. This flask contains artificial violet scent, called ionone, discovered in the Berlin University Institute by Professor F. Tiemann, and made by Haarmann and Reimer, of Holzminden. The contents of this flask would be sufficient to envelope not only the lecture theatre but also the whole street "Unter den Linden" in a cloud of violet scent, for its odour is extraordinarily strong.

Unlike the simple ionone most natural odours of flowers are complicated mixtures of perfumes. Nevertheless their reproduction has been successfully undertaken. Amongst the flower scents here before you are may, jasmine, elder, tuberose, and finally the greatest rarity—artificial rose oil. Although the natural oil contains more than a dozen and a half different aromatic substances, the chemists of the Leipzig Perfumery Company (Heine and Co., Schimmel and Co.) have, after long researches, succeeded in isolating all these constituents, preparing each one artificially, or obtaining them from other cheap oils, and putting them together in the right proportions. It requires a very sensitive nose to discriminate between the artificial product and the natural rose oil.

I only hope that the noble patroness of roses, Her Majesty the Empress, will not take it ill that chemical synthesis should thus attack the monopoly of her favourites. Perhaps she will be placated if your Majesty will graciously take a specimen of the artificial product and offer it to Her Majesty the Empress as a present from chemical industry.

These examples show how successfully organic synthesis has endeavoured to dabble in nature's handiwork. What I have said will also serve to show that chemistry, and with it all natural knowledge, is the true land of unlimited possibilities. To the exploration of this land and the removal of the treasures concealed in it the Kaiser Wilhelm Institute will devote itself in the future. But we must not expect that it will do everything and will quite displace other institutes. We older institutions do not feel by any means so feeble as to allow that. On the contrary, we shall exert our best endeavours to compete vigorously with the young institute, which will keep us both on the alert.

But there can be no doubt that the godchildren of the German Kaiser in the fresh healthy air of the Grunewald, and through the generous provision of their benefactors, will develop lustily and become renowned investigators.

Thus we may confidently hope that posterity will regard the founding of the Kaiser William Gesellschaft as a blessing for the fostering of scientific investigation in Germany.

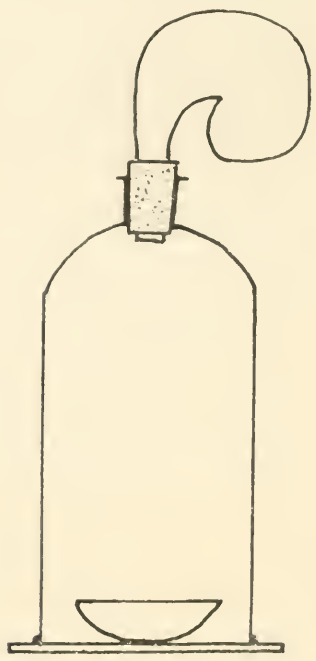
Rationality of the Ratios of the Magnetic Moments of the Atoms and a New Universal Constituent of Matter.—Pierre Weiss.—The author gives a list of the magnetic moments of the gram-atoms, and shows that the values obtained by different investigators all point to the existence of a common constituent or element in the different atoms. This element the author calls magneton. It is present in the atoms of iron, nickel, cobalt, manganese, uranium, and the metals of the rare earths.—*Comptes Rendus*, clii., No. 4.

A SUBLIMATION APPARATUS.

By R. WRIGHT.

By means of this simple apparatus sublimations may be carried out with small loss of material, and in the case of those substances—such as iodine—whose vapours are of an irritating nature, without the usual inconvenience to the operator.

The apparatus consists of a narrow bell-jar, fitted with a cork through which passes the delivery tube of a small glass retort, the tube being cut off fairly short. The sub-



stance to be sublimed is placed in the retort, which is then connected with the bell-jar, and the whole inverted over a watch-glass or small porcelain dish resting on a few thicknesses of moist filter-paper laid on a tile.

On gently heating the retort bulb the substance sublimes and collects in the dish. Slow heating is necessary, otherwise the substance may be deposited on the sides of the jar.

By placing the jar on a ground glass plate and connecting with a pump by means of an extra tube through the cork, sublimations may be carried out *in vacuo*.

THE CORROSION OF IRON.

A HISTORICAL CORRECTION.

By J. NEWTON FRIEND.

THE problem of the corrosion of iron is one which, during the past few years, has been absorbing the attention of numerous investigators. It is now universally acknowledged that of the five theories which have been advanced to account for the phenomena, only two are to be regarded as meriting our serious attention. These are "The Electrolytic Theory," originated by Whitney in 1903, and the "Acid Theory." The more recent researches of Moody and the writer clearly show that of the two the latter, namely, the acid theory, is the correct one. The question naturally arises, therefore, as to who was the originator of this theory. The majority of writers (see Lambert and Thomson, *Trans. Chem. Soc.*, 1910, xcvii. 2426; "T.M.L.," *Nature*, March 2, p. 25; and many others) attribute the honour to Crum Brown, and refer to his classical paper read before the Iron and Steel Institute of London in 1888. I do not know if authors ever read this original paper, or simply quoted the reference one from the other, but facts of the case are these:—Prof. Crum Brown was not the author of the "Acid Theory of Corrosion," and, what is more important still, *he never claims to be*. Now, it is not the writer's desire to belittle the work of Crum Brown; on the contrary, I admit with pleasure that his paper embodies the clearest and most scientific expression of the acid theory which had then received publication; but it was the expression of the generally accepted theory of the day, and was not in itself new. No fewer than eighteen years previously, namely, in 1870, Crace Calvert performed a number of experiments from which he concluded that an acid (carbonic acid) was essential to corrosion, and he gave a full account of his work in a classical memoir read before the Manchester Literary and Philosophical Society on January 24th, 1871. This would appear to be the first published account of the acid theory of corrosion, as such. But a careful study of still earlier literature almost convinces the reader that the writers were possessed of—to say the very least—a hazy notion that an acid was essential to corrosion. Thus the great Swedish chemist, Benzelius, drew attention to the fact that iron would not corrode in the presence of caustic soda—a fact which, until quite recently, was held to be an indisputable argument in favour of the acid theory. Payen (1837), Mallet (1838), Adie (1845), and others were evidently aware that corrosion was not the simple case of oxidation, as Kuhlmann seems to have been one of the first to suggest.

It would appear, therefore, that the formulation of the acid theory of corrosion was one of gradual development up to the time of Crace Calvert, and that this investigator was the first to give clear expression to the same in 1871. The literature on the subject of the corrosion of iron is not only so vast, but so widely scattered, that numerous mistakes of this kind have arisen, and many researches appear to have been lost sight of, in so much that modern investigators have frequently spent a considerable amount of time in studying problems that had already been worked out seventy or eighty years ago. With a view to correcting these errors, and to assist future workers in learning what has already been done, the present writer has made a special study of the history of the corrosion of iron, and has embodied the results in a book which is now in the press (Messrs. Longmans and Co.), and will appear shortly.

The Technical College, Darlington.

NOTE ON KJELDAHL'S PROCESS.

By VINCENT EDWARDS, F.I.C., and DUDLEY CHADS.

This excellent process now so essential for the estimation of nitrogen in all forms has one or two drawbacks, without counting the complete breakdown of the distilling flask, which can be obviated by using a copper vessel as suggested by one of us some years ago. We refer to the "bumping," and also, in cases where nitrates are being estimated, the troublesome frothing. To prevent the first of these the time-honoured granulated zinc is used. This, however, though it does reduce the "bumping," seems to increase the frothing, possibly by the too energetic liberation of hydrogen. We have recently employed granulated tin in place of zinc, and the general smoothness of the operation seems considerably increased. Small as this variation may seem it is of importance, as without doubt the "bumping," frothing, and "boiling over" are the weak points in this most useful method.

Barking, March 4, 1911.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 2nd, 1911.

Sir Alexander Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Reversal of the Reflex Effect of an Afferent Nerve by Altering the Character of the Electrical Stimulus Applied.*" By Prof. C. S. Sherrington, F.R.S., and Miss S. C. Sowton.

"*Carbon Dioxide Output during Decerebrate Rigidity.*" (Preliminary Communication). By H. E. Roaf, D.Sc.

"*Alcoholic Ferment of Yeast-juice.* Part VI. *Influence of Arsenates and Arsenites on the Fermentation of the Sugars by Yeast-juice.*" By Arthur Harden, F.R.S., and W. J. Young.

The results of the investigation may be summarised as follows:—

1. When a suitable amount of arsenate is added to a fermenting mixture of yeast-juice and a sugar, it causes a large acceleration in the rate of production of carbon dioxide and alcohol. This enhanced rate differs from that produced by phosphate, inasmuch as it continues long after a chemical equivalent of carbon dioxide has been evolved. The arsenate, moreover, is found in the free state throughout the fermentation.

2. The rate attained increases rapidly with addition of arsenate until *optimum* concentration is reached, after which it decreases, at first rapidly and then more slowly.

3. The total fermentation produced depends on the particular concentration of arsenate employed and may be either higher or lower than that given in the absence of arsenate. As the high rate produced by a suitable quantity of arsenate persists for a long time, very considerable increases in the total fermentation may be observed.

4. Glucose and mannose are similarly affected by yeast-juice in presence of arsenate, whereas fructose is much more rapidly fermented than these two sugars, and the optimum concentration of arsenate in its presence is greater.

5. The increased rate of fermentation of sugars in presence of arsenate is due to an acceleration of the rate of action of the hexosephosphatase of the juice, whereby an increased supply of phosphate is afforded. The action is therefore essentially different from that of phosphate, and it has been found that arsenate cannot replace phosphate in the fundamental reaction of alcoholic fermentation.

6. Arsenate also causes a considerable increase in the rate of autofermentation of yeast-juice and in the rate of fermentation of glycogen. This is mainly due to acceleration of the rate of action of the diastatic enzyme of yeast-juice (glycogenase).

7. The action of arsenites is similar to that of arsenates, but is much less marked.

8. Both arsenate and arsenite cause total inhibition of the fermentation when they are present in a high concentration, but the nature of this effect has not been ascertained.

"*Experiments to ascertain if certain Tabanidæ act as the Carriers of* Trypanosoma pecorum." By Colonel Sir David Bruce, C.B., F.R.S., A.M.S.; and Captains A. E. Hamerton, D.S.O., and H. R. Bateman, R.A.M.C. (Sleeping Sickness Commission of the Royal Society, Uganda, 1908-10).

"*Experimental Studies in Indian Cottons.*" By H. M. Leake.

CHEMICAL SOCIETY.

Ordinary Meeting, March 2nd, 1911.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. Frank H Plews, C. F. Yates, and Thomas Callen were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Thomas Eggington, B.Sc., The Hawthorns, Ibstock, Leicester; Arthur Alfred Eldridge, B.Sc., School House, Alpha Road, Surbiton Hill; Edwin Burnhope Hughes, 5, Perham Road, West Kensington, W.; Leonard Owen Newton, St. Elba, Napoleon Road, St. Margaret's-on-Thames; Eric Everard Walker, 210, Bedford Hill, Balham, S.W.; Henry Hough Watson, Braystones, via Carnforth; William Wood, Katoomba, King Edward Avenue, Dartford.

A ballot for the election of Honorary and Foreign Members was held, and the following were subsequently declared duly elected:—Prof. Dr. Eugen Bamberger (Zürich), Prof. Giacomo Ciamician (Bologna), Prof. Dr. Paul Heinrich Ritter von Groth (Munich), Prof. John William Mallet (Virginia), Prof. Dr. Walther Nernst (Berlin).

The President announced that the Royal Academy of Sciences of Turin had given notice of the founding of a Vallauri Prize of 26,000 lire for the most important work in the domain of the physical sciences published during the period January 1st, 1915, to December 31st, 1918.

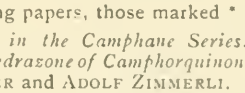
The President read the names of the Fellows recommended by the Council for election as Officers and Ordinary Members of Council for the year 1911 to 1912.

Of the following papers, those marked * were read:—

*53. "*Studies in the Camphane Series.* Part XXIX. *A New Phenylhydrazone of Camphorquinone.*" By Martin Onslow Forster and Adolf Zimmerli.

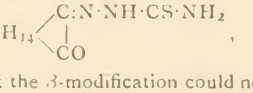
The constitution of camphorquinonephenylhydrazone has been the subject of much speculation. Following their investigation of the hydrazones, semicarbazones, and phenylcarbamylhydrazones of camphorquinone, each of which was obtained in two interconvertible isomeric modifications, the authors have transformed the known camphorquinonephenylhydrazine into an isomeride, which stands in the same relation to the existing derivative as the β-members of the other pairs do to the respective α-compounds; they regard the isomerism as stereo-chemical.

Camphorquinone-β-phenylhydrazone,—

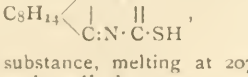


prepared by heating the α-modification, is a bright yellow crystalline substance, melting at 36°; it dissolves very readily in organic media, including petroleum. The 1 per cent solution in alcohol has $[\alpha]_D$ 375°, which is raised to 397° by heating the liquid during twelve hours at 63°; under the same treatment the rotatory power of the α-phenylhydrazone falls from $[\alpha]_D$ 431° to 398°.

Camphorquinone-α-thiosemicarbazone.—



melts at 174°, but the β-modification could not be isolated, being transformed too rapidly into *camphane-thiotriazine*,



a bright yellow substance, melting at 207°. *Camphorquinonephenylthiocarbamylhydrazone*,—

prepared from both camphorquinonehydrazones and phenylthiocarbimide, melts at 184°.

Discussion.

The President asked whether there was any explanation of the great difference observed between the melting-points of the α- and β-forms of the phenylhydrazone derivatives.

Mr. W. Robertson submitted that the isolation of a second form of camphorquinonephenylhydrazone of low melting-point and high rotatory power was not necessarily at variance with the conclusion drawn from the mutarotation measurements that, in benzene solution, a labile form of practically no optical activity was present. The results could be harmonised by supposing the existence of three isomerides in alcoholic solution, the α-form (m. p. 190°) first undergoing a rapid change into a second form (this being the change examined in the non-ionising purified benzene), the second form then changing relatively slowly into the β-form (m. p. 36°), a conclusion supported by solubility measurements (*Trans.*, 1905, lxxxvii., 1299).

It was also pointed out, in reply to Dr. Forster, that in Armstrong and Robertson's paper, the colouring material in solution was due to the complex, $C{:}N{\cdot}NH{\cdot}C_6H_5$ | , and the opinion was expressed that the CO amount of this form present was small (*loc. cit.*, p. 1278).

Dr. Veley expressed the opinion that the observed differences in the algebraical sum of the factors of chemical change (namely, the values of $K + K_1$) were probably due to the presence of a small quantity of the β-hydrazone in the α-derivative, which accelerated the transformation of the former into the latter compound. The case would be perfectly analogous to the acceleration observed in the transformation of rhombic into monosymmetric sulphur, of cyanic acid into cyamelide, and of the oxidation of oxalic acid by acid permanganate as effected by the presence of manganese sulphate. The explanation thus offered was probably identical with that proposed by Prof. Walker, though stated in a somewhat different form.

Dr. Lowry supported the view that three isomeric hydrazones of camphorquinone must now be recognised, the ordinary form of the compound being converted quickly at atmospheric temperatures (to the extent of 10 per cent) into an isomeride of very low rotatory power, and slowly at a higher temperature (to the extent or about 50 per cent) into the new isomeride described by Dr. Forster. An analogous case was that of nitrocamphor, which changed quickly (to the extent of one-sixth) into the acidic pseudo-nitro-compound, but could be forced to undergo a further change of the Beckmann type, giving rise to a third isomeride, namely, camphoryloxime. Although the less stable isomerides could not be isolated, their existence in solution had been demonstrated by precisely the same methods as in the case of such well known substances as gluconic and galactonic acids, which decomposed into lactone and water as soon as any attempt was made to separate them from their solutions.

Prof. Green remarked that the greater depth of colour of the β-isomeride, as compared with that of the α-isomeride, would be well explained by the *anti-* and *syn*-formulæ suggested by the authors, since the proximity of the NH-group to the CO-group in the *syn*-modification would favour a dynamic keto-enolic oscillation.

Dr. Forster, replying to the President, pointed out that the isomeric benzaldoximes melted at 35° and 128° respectively; moreover, the difference between the melting-points of maleic and fumaric acids is 156°, greater therefore than that which separates the phenylhydrazones of camphorquinone. The necessity of now recognising three isomerides, claimed by Mr. Robertson and Dr. Lowry, was not accepted by the authors, who regarded Mr. Robertson's solubility experiments as capable of explanation by the new facts brought to light. Without denying that future investigation might reveal a third isomeride, it was difficult to recognise any justification for stating that it would be optically inactive. Dr. Forster agreed with Mr. Robertson's second point, namely, that in the latter's paper with Prof. Armstrong, a material owing its colour to the complex $C{:}N{\cdot}NH{\cdot}C_6H_5$ was stated to be present in very small proportion, but reminded Mr. Robertson that the evidence furnished for its existence was limited to the bare statement of its occurrence; moreover, the yellow substance was entirely ignored in the later parts of their paper, which dealt only with the hypothetical, colourless "metameride having little, if any, optical activity."

*54. "*Fluorone Derivatives.*" By Frank George Pope and Hubert Howard.

Phosphorus pentachloride converts 3-hydroxy-9-phenylfluorone into 3 : 6-*dichloro*-9-*phenylxanthonium chloride*, an extremely reactive compound, which condenses readily with amines to produce compounds of the rosamine type, with potassium cyanide and with sodium ethoxide to form cyanoxanthen and xanthyl ethers respectively. Reasons were given for preferring a paraquinonoid configuration for the fluorones; *phenylfluorone* and *phenylnaphthafluorone* were also described.

Discussion.

Prof. Green said that the fluoran dye-stuffs seemed to occupy an intermediate position between the ortho-quinonoid and the para-quinonoid dye-stuffs, and from many facts he was disposed to believe that they were usually in a state of oscillation between the two forms, or that they readily changed from one form to the other. In certain cases, as had been shown for quinolphthalein by Green and King, an ortho-quinonoid structure must be assumed.

*55. "*The Constituents of* Withania somnifera." By Frederick Belding Power and Arthur Henry Salway.

The material employed for this investigation represented the entire plant of *Withania somnifera*, Dunal (Nat. Ord. *Solanaceae*), and was obtained directly from South Africa. Both the roots and the overground portion of the plant responded to the tests for an alkaloid, and they were separately examined.

The investigation has shown that a number of substances present in the root are likewise contained in the leaves and stems of the plant. These substances, besides small amounts of an essential oil and a sugar yielding *d*-phenylglucosazone, were as follows:—Hentriacontane, $C_{31}H_{64}$; a phytosterol, $C_{27}H_{46}O$; palmitic, stearic, cerotic, oleic, and linolic acids; and ipuranol, $C_{23}H_{38}O_2(OH)_2$. From the root there were obtained, furthermore, a new monohydric alcohol, *withaniol*, $C_{25}H_{33}O_4{\cdot}OH$, decomposing at 305°, and having $[\alpha]_D$ +91·2°, and an amorphous alkaloidal principle, which, on treatment with alkali hydroxides, yielded a crystalline *base*, $C_{12}H_{16}N_2$ (m. p. 116°). The leaves and stems yielded the following new compounds:—A monohydric alcohol, *somnirol*, $C_{32}H_{43}O_6{\cdot}OH$, decomposing at 205°, and having $[\alpha]_D$ +34·8°; a dihydric alcohol, *somnitol*, $C_{33}H_{44}O_5(OH)_2$, decomposing at about 250°, and having $[\alpha]_D$ +21·2°; and an acidic hydrolytic product, *withanic acid*, $C_{29}H_{45}O_6{\cdot}CO_2H$ (m. p. 226°), the *methyl* ester of which decomposed at 255°.

Withania somnifera, unlike some other solanaceous plants, contains no mydriatic alkaloid, and physiological tests, conducted on a dog, failed to confirm the sedative or hypnotic properties attributed to it.

*56. "*The Carbohydrate Constituents of Pára Rubber: Separation of* l-*Methylinositol.*" (Preliminary Note). By Samuel Shrowder Pickles and Bernard Wyndham Whitfeild.

During the examination of various specimens of smoked plantation rubber from the Malay Peninsula, the presence of a crystalline sugar-like substance, melting at 191 – 192°, was detected in all cases. The amount of this constituent present in the different specimens varied considerably, being in some cases as high as 2·5 per cent. On analysis it gave the following results:—

(1) 0·1674 gave 0·2648 CO_2 and 0·1035 H_2O. C = 43·1 ; H = 6·9.

(2) 0·2150 gave 0·3385 CO_2 and 0·1350 H_2O. C = 42·9 ; H = 7·0.

(3) 0·2225 gave 0·2615 AgI. OMe = 15·5

$C_6H_{11}O_5$·OMe requires C = 43·3 ; H = 7·2 ; OMe = 15·96 per cent.

This substance is lævorotatory ; a 10 per cent aqueous solution gave α −8°, whence $[\alpha]_D$ 80°. It does not reduce Fehling's solution, and is scarcely affected by prolonged boiling with moderately concentrated sulphuric or hydrochloric acids. Hydriodic acid decomposes it with the formation of methyl iodide and *l*-inositol (m. p. 237).

The compound is thus *l*-methylinositol, and is identical with that isolated from quebracho bark by Tanret (*Comptes Rendus*, 1889, cix., 908), and designated quebrachite. Its presence has also been previously observed in the aqueous portion of the latex of *Hevea brasiliensis* which remains after the coagulation of the rubber, by de Jong (*Rec. Trav. Chim.*, 1906, xxv., 48).

The authors have also confirmed this observation by the examination of specimens of the latex of *Hevea brasiliensis* from the Botanic Gardens at Singapore, and have found that this substance (*l*-methylinositol) constitutes the greater portion of the carbohydrate constituents of the latex. They also find that the occurrence of *l*-methylinositol (quebrachitol) is quite general in rubbers from *Hevea brasiliensis*, and have isolated it, not only from those of Asiatic origin, but also from "fine hard Pára" rubber from South America.

Discussion.

Dr. Pickles stated, in reply to questions, that, although probably the *l*-methylinositol in the latex was not directly connected with the formation of rubber, its presence was worthy of note, and there was the possibility that under the influence of enzymes it might be converted into products which could be utilised by the plant for the construction of the rubber hydrocarbon.

57. "*Potassium Cupricarbonates.*" By S. U. Pickering.

Previous work on other cupri-compounds indicate the possibility of there being eight, or even more, compounds of potassium carbonate with copper carbonate ; nine have been isolated. Potassio-cupric carbonate exists in a hydrated and anhydrous condition, the latter, however, not being the compound of the same empirical formula isolated by Reynolds (*Trans.*, 1898, lxxiii., 263). The β-cupricarbonate, $(CO_3)_2K_2Cu^{IV},H_2O$, forms a gelatinous precipitate ; and a compound which appears to be derived from it by abstraction of the elements of water (indirectly) has been obtained. The other five compounds, which are all crystalline, are α-cupricarbonates (that is, containing the $Cu^{IV}CO_3$ group), with the formulæ : $[(CO_3)_3K_2Cu_2^{IV},Cu_2(CO_3)_2]$, $[(CO_3)_4K_4Cu_2^{IV},CuK_2(CO_3)_2]$, and $(CO_3)_4K_4Cu_2^{IV},Cu_2K_2(CO_3)_3]$, with two other members derived from the last by the substitution of Cu for K_2.

Three of these substances have the empirical formula $CuK_2(CO_3)_2$, but are well distinguished from each other by their physical and chemical properties, and by their heats of formation. Several other organic acids apparently form cupri-compounds analogous to the cupricarbonates.

58. "*Synthesis of Dipeptides of α-Aminolauric Acid with Glycine, Alanine, Valine, Leucine, and Asparagine.*" By Arthur Hopwood and Charles Weizmann.

In view of the possible presence of peptides of α-aminolauric acid with amino-acids in the proteins occurring in certain plants, the authors have prepared the following derivatives :—

α-Bromolauryl chloride, $C_{11}H_{22}Br{\cdot}COCl$, is obtained by heating α-bromolauric acid with phosphorus pentachloride. It is a colourless liquid, boiling at 150°/10 mm.

α-Bromolaurylglycine, $C_{11}H_{22}Br{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, is prepared by the interaction of α-bromolauryl chloride and glycine in presence of sodium hydroxide. It forms colourless rhombic plates, melting at 117·0° to 118·5°, which are only sparingly soluble in water, but readily so in alcohol, ether, benzene, toluene, or alkalis.

α-Aminolaurylglycine, $NH_2{\cdot}C_{11}H_{22}{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, is formed by heating α-bromolaurylglycine with concentrated aqueous ammonia. It crystallises in prismatic needles, which sinter at 207°, and melt and decompose at 214·0—214·5 . It is nearly insoluble in water, sparingly soluble in alcohol, but readily so in alkalis or acids. Like the proteins, it yields a white amorphous precipitate with phosphotungstic acid, and is hydrolysed by enzymes.

Somewhat similar bromo-compounds are obtained by the condensation of α-bromolauryl chloride with alanine, valine, leucine, and asparagine, and these, on treatment with ammonia, yield the corresponding dipeptides.

59. "*The Occlusion of Hydrogen by the Palladium-gold Alloys.*" By Arthur John Berry.

Determinations have been made of the quantities of hydrogen occluded by the palladium-gold alloys when charged electrolytically with hydrogen. With alloys in which the concentration of palladium exceeded about 25 per cent, the occluding power was found to be a simple function of the concentration of that metal. Alloys more dilute in respect to palladium do not possess the property of occluding any hydrogen.

60. "*Synthesis of* dl-3 : 4-*Dihydroxyphenylalanine.*" By Casimir Funk.

With the view of testing whether any relationship exists between tyrosine and adrenaline, a catechol derivative corresponding with tyrosine was prepared. The synthesis of this *dl*-3 : 4-*dihydroxyphenylalanine* was carried out according to the method originally suggested by Erlenmeyer. The cyclic carbonic ester of catecholaldehyde was condensed with hippuric acid, and the resulting azlactone saponified with sodium hydroxide ; the substituted cinnamic acid which was formed was reduced with sodium amalgam, and the benzoyl group eliminated by boiling with hydrochloric acid. The amino-acid obtained gave all the ordinary chemical reactions of adrenaline. Experiments are now being conducted with the view of ascertaining the nature of the changes which this substance undergoes in the animal body.

61. "*The Interaction of Chlorine and Carbon Monoxide.*" (Preliminary Note). By David Leonard Chapman and Frank Houghton Gee.

It has been shown that the photochemical interaction of carbon monoxide and chlorine is inhibited by the same substances as those which prevent or retard the action between chlorine and hydrogen in light. Nitrosyl chloride almost prevents the union of carbon monoxide and chlorine when the mixed gases are exposed to a very intense light, and since it is not decomposed its action continues for an indefinite period.

Experiments have also been performed at higher temperatures ; the gases combine slowly at 350°, and it is significant that light has no—or, at most, an inappreciable—influence on the rate of combination at this temperature. The inhibitors which have been tried, namely, nitrosyl chloride and oxygen, are also without effect on the pyrogenic union of the gases. The experiments are being continued over a wider range of temperature.

62. "*Experiments on the Synthesis of the Terpenes.* Part XVI. *Resolution of* dl-1-*Methyl*-Δ^3-cyclo*hexene*-3-*carboxylic Acid. Synthesis of the* d- *and* l-*Modification of* Δ^3-m-*Menthenol*(8) *and* $\Delta^{3:8(9)}$-m-*Menthadiene.*" By Bernard Dunstan Wilkinson Luff and William Henry Perkin, jun.

The authors have succeeded in resolving *dl*-1-methyl Δ^3-*cyclo*-hexene-3-carboxylic acid :—

$$CHMe\begin{cases}CH_2{\cdot}C(CO_2H)\\ CH_2\text{——}CH_2\end{cases}\!\!>CH,$$

by the use of brucine and *l*-menthylamine, whereby the

synthesis of the *d*- and *l*-modification of Δ^3-*m*-menthenol(8) and $\Delta^{3:8(9)}$-*m*-menthadiene has been made possible.

63. "*Experiments on the Synthesis of the Terpenes.* Part XVI. d-Δ^3-p-*Menthenol*(8) *and* d-$\Delta^{3:8(9)}$-p-*Menthadiene*." By TSAN QUO CHOU and WILLIAM HENRY PERKIN, jun.

The preparation of *d*-1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid—

$$CHMe<\begin{matrix}CH_2—CH\\CH_2\cdot CH_2\end{matrix}>C\cdot CO_2H,$$

from *d*-1 methyl*cyclo*hexan-3-one was described. It has $[\alpha]_D$ +150°1', and yields the *d* modification of Δ^3-p-*menthenol*(8) and $\Delta^{3:8(9)}$-p *menthadiene* when its ester is treated with magnesium methyl iodide and subsequently with dehydrating agents.

64. "*Some Derivatives of o-Veratraldehyde.*" (Preliminary Note). By WILLIAM HENRY PERKIN, jun., WALTER MORRELL ROBERTS, and ROBERT ROBINSON.

o-Veratraldehyde, $(MeO)_2C_6H_3\cdot CHO$ MeO:MeO:CHO 1 : 2 : 3, is a substance of importance in connection with the synthesis of alkaloids, and particularly of berberine. The authors have therefore prepared some of its more interesting derivatives.

o-Veratric acid, $C_6H_3(OMe)_2\cdot CO_2H$, is obtained on oxidation of the aldehyde in acetone solution with potassium permanganate. It is moderately readily soluble in hot water, and crystallises in needles, melting at 122°. Its methyl ester melts at 47°, and has also been prepared by Fritsch (*Annalen*, 1898, ccci., 356) by the methylation of guaiacolcarboxylic acid.

1 : 3-*Diketo*-2-*o*-*veratrylidenehydrindene*—

$$C_6H_3(OMe)_2\cdot CH:C<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

is prepared by heating together the aldehyde and diketohydrindene. It crystallises from alcohol in bright yellow needles, melting at 160°.

5 : 6-*Dimethoxy*-2-*o*-*veratrylidene*-1-*hydrindone*—

$$C_6H_3(OMe)_2\cdot CH:C<\begin{matrix}CO\\CH_2\end{matrix}>C_6H_2(OMe)_2,$$

is obtained when a solution of equimolecular proportions of *o*-veratraldehyde and 5 : 6-dimethoxy-1-hydrindone in ethyl alcohol is treated with two or three drops of concentrated potassium hydroxide. The substance crystallises from alcohol in pale yellow needles, melting at 186°. When it is dissolved in sulphuric acid, an orange-coloured solution is obtained, which contains the anhydrosulphate of a pyranol base produced with loss of methyl alcohol.

2:3-*Dimethoxycinnamic Acid*, $C_6H_3(OMe)_2\cdot CH:CH\cdot CO_2H$. —This substance is best prepared by hydrolysis of the corresponding ethyl ester obtained by the condensation of *o*-veratraldehyde with ethyl acetate by means of sodium.

The acid separates from ethyl acetate in long colourless needles, and melts at 180°. It shows the usual properties of a cinnamic acid, and is readily reduced by sodium amalgam, yielding 2 : 3-*dimethoxy*-β-*phenylpropionic acid*, $C_6H_3(MeO)_2\cdot CH_2\cdot CH_2\cdot CO_2H$, which crystallises from a mixture of benzene and light petroleum in prisms, melting at 69°.

4:5-*Dimethoxy*-1-*hydrindone*, $C_6H_2(OMe)_2<\begin{matrix}CO\\CH_2\end{matrix}>CH_2$,

is produced in good yield when dimethoxyphenylpropionic acid is treated with phosphoric oxide in boiling benzene solution. It crystallises from ether or light petroleum in small pale yellow plates, melting at 82°.

4 : 5-*Dimethoxy*-2-*o*-*anisylidene*-1-*hydrindone*,

$$C_6H_2(OMe)_2<\begin{matrix}CO\\CH_2\end{matrix}>C:CH\cdot C_6H_4\cdot OMe,$$

prepared by heating equimolecular proportions of anisaldehyde and 4 : 5-dimethoxy-1-hydrindone with potassium hydroxide in warm alcoholic solution, crystallises from acetic acid or ethyl alcohol in long feathery needles, melting at 153—154°.

2-iso*Nitroso*-4 : 5-*dimethoxy*-1-*hydrindone*,

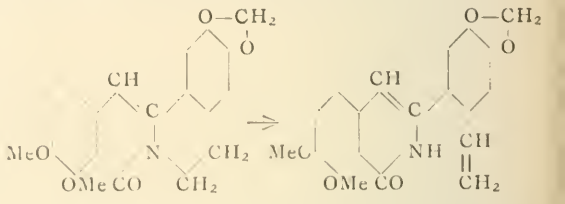
$$C_6H_2(OMe)_2<\begin{matrix}CO\\CH_2\end{matrix}>C:N\cdot OH,$$

is prepared by the action of amyl nitrite and a few drops of hydrochloric acid at 50° on the hydrindone dissolved in ethyl alcohol. It forms pale yellow needles which melt and decompose at 244°, and is soluble in alkalis. On oxidation with potassium permanganate in alkaline solution, a good yield of hemipinic acid is obtained.

65. "iso*Oxyberberine*." (Preliminary Note). By NORMAN BLAND, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

When oxyberberine is heated in an autoclave at 130° for five hours with dilute hydrochloric acid, it is converted into an isomeride to which the name iso*oxyberberine* is given.

The new substance is probably produced in accordance with the following scheme, which represents *iso*oxyberberine as a derivative of *iso*carbostyril :—



*iso*Oxyberberine is much less soluble in glacial acetic acid than is oxyberberine, and crystallises from this solvent in pale greyish yellow microscopic needles melting at 245°.

It gives a red azo-colouring matter when treated with alkali and diazotised sulphanilic acid, and a purplish red colour with aqueous ferric chloride. It does not appear to have basic properties.

*Acetyliso*oxyberberine, $C_{20}H_{16}O_5N(CO\cdot CH_3)$, is prepared by boiling *iso*oxyberberine with acetic anhydride and sodium acetate. It crystallises from acetic acid in needles, and melts at 261°.

*Nitroso*iso*oxyberberine*, $NO\cdot C_{20}H_{16}O_5N$, is prepared by shaking *iso*oxyberberine with a solution of amyl nitrite in glacial acetic acid for five hours in the cold. The compound is very sparingly soluble in most organic solvents, but can be re-crystallised from hot pyridine, and occurs in highly characteristic, golden brown, microscopic needles, melting at 263—265°. These and other derivatives of this substance are in process of detailed investigation.

66. "*The Application of Viscometry to the Measurement of Rate of Reaction.*" By ALBERT ERNEST DUNSTAN and ALBERT GEORGE MUSSELL.

The authors have measured the viscosity of a variety of compounds undergoing chemical changes. They find that, in general, the viscosity changes with the lapse of time, in such a way that the total viscosity change is proportional to the amount of substance transformed. They consider that a useful method for the measurement of the velocity of reaction may be based on this observation. Accordingly, experiments have been made in which the rates of the following transmutations are measured :—

Freshly distilled acetoacetic ester ⇌ equilibrium mixture ; aniline and ammonium thiocyanate ⇌ phenylthiocarbamide ; ammonium cyanate ⇌ carbamide ; ammonium thiocyanate ⇌ thiocarbamide ; acetic anhydride and water ⇌ acetic acid ; benzoyl chloride and water ⇌ benzoic acid.

67. "*The Action of Hydrogen Sulphide on the Alkyloxides of the Metals.* Part I. *Sodium and Potassium Ethoxides*." By ALEXANDER RULE,

The author has undertaken this investigation in the hope of preparing the sulphides of aluminium, chromium, and ferric iron by precipitation from alcoholic solution. These sulphides cannot be prepared from aqueous solutions, owing to hydrolysis, and when obtained in the dry way

they are always impure. As no record of the action of hydrogen sulphide on the alkyloxides of sodium or potassium could be discovered, this action was first investigated, and found to result in the formation of the pure anhydrous hydrosulphides of these metals, the compounds being precipitated from alcoholic solution on the addition of ether or benzene.

The reaction provides a very simple and rapid method for the preparation of the anhydrous hydrosulphides, and the yields are practically quantitative.

The behaviour of hydrogen sulphide towards the solid ethoxides of sodium and potassium was also investigated. Reaction was found to take place at the ordinary temperature, and resulted in the formation of the hydrosulphides of the metals and evolution of alcohol.

68. "*Simple Method of Decomposing Refractory Tin Ores.*" By Herbert Yabsley Loram.

The mineral (2 grms., or more if desired), crushed to a sixty-hole powder, is fused for about an hour in a covered silver crucible at a temperature well below its melting-point, with about six or seven times its weight of potassium hydroxide, to which is added potassium cyanide equal to the weight of tin ore taken.

The mass, on cooling, is extracted with water, when the whole will dissolve in dilute hydrochloric acid, and after boiling to destroy any cyanide still remaining, the tin can be estimated by any of the usual methods.

ROYAL PHOTOGRAPHIC SOCIETY.

Mr. Chapman Jones read an important paper before the Royal Photographic Society on March 7th, dealing with the relationship between the size of the particles of silver embedded in the gelatin film and the colour of the photographic image.

Many explanations had been urged, he said, for differences of colour obtained in the image, one of the most plausible being that it was the distance apart of the particles which determined the colour. It was Mr. Chapman Jones's conclusion, however, that the average size of the image-forming particle, and that alone, was the determining factor. He found that the colour effects were independent of the nature of the material of the particle, nor did the method of production of the particles affect the result. Also, there was no relation whatever between the distance of the particles apart and the colour effect, unless, indeed, the distance between particles was so considerably reduced as to make certain of them almost coalesce, and the little group act as though it were one particle. But the relationship between the size of the particle and the light that was lost or scattered was an intimate one and held good throughout his researches upon the subject. The enlargement of the particles always affected the colour of the film, an orange tint, for instance, becoming brown or brownish grey after enlargement. He had not employed the ultra-microscope method, but he had enlarged the silver particles up by applying the intensifying action of mercuric chloride and ferrous oxalate. The smallest particles gave no colour effect whatever, and the colour afterwards obtained varied with the process of enlargement from yellow to orange, then to pink, brownish-yellow, yellowish-red, brown-orange, to purplish-grey. The particles began to be just visible microsopically when of a size of 0·114 microns, feebly visible at 0·17, and fairly visible at 0·20. When the particle only represented in diameter a quarter of a wave-length in the ultra-violet no colour effect whatever was obtained, but when the particles in diameter became equal to half a wave-length of certain of the colour-rays in the spectrum, colour disturbances began to be manifest. The diameter of the particle bore a certain relationship to the wave-length of the light that was scattered. It seemed natural to suppose that if an obstruction in the shape of a minute particle of half a wave-length in diameter were introduced it might tend to stop or dampen the wave, and while affecting those waves the length of which was twice its own diameter would leave untouched other larger or smaller waves, thereby influencing the colour of the transmitted light. It was not necessary for a particle to be quite equal to a whole wave-length in order to be an effective block. Mr. Chapman Jones said that he only put this forward as a suggestion, but it did seem to fit in with the measurements by which a particle of a diameter of half a wave-length was shown to begin to affect the colour. In short, the size of the particle seemed to be the determining factor in selective scattering, and the light was scattered by particles approximating in diameter to half a wave-length of the scattered light.

NOTICES OF BOOKS.

Inorganic Chemistry for Advanced Students. By the Right Hon. Sir Henry Roscoe, F.R.S., D.C.L., LL.D., and Arthur Harden, F.R.S., Ph.D., D.Sc. (Vict.). Second Edition. London: Macmillan and Co., Ltd. 1910. (4s. 6d.).

This book is not intended for beginners, but for the use of those who have done some elementary work in inorganic chemistry, and require a more advanced course before proceeding to specialise in the science. It gives a clear account of the descriptive chemistry of the non-metals and the commoner metals, and illustrative experiments are interspersed throughout the text. The theory of chemistry is treated adequately, and to the second edition chapters have been added on some subjects which have seen specially rapid development recently; for example, technical chemistry and radio-activity. The book is so excellently systematic that it would be a valuable aid to students who are preparing for examinations, and the summaries of each chapter and the questions on the text are features which will specially commend themselves to both student and teacher.

The Mineralogy of Arizona. By F. N. Guild. Easton, Pa.: The Chemical Publishing Co. London,: Williams and Norgate. 1910.

The abundant mineral wealth of Arizona is fully described in this book, and the mode of occurrence and chemical composition of practically all the minerals which have been found in its mountains and cañons are discussed. From the nature of the book it represents little more than a compilation from various sources, but the work of gathering together the material for it appears to have been carefully done, and a considerable degree of completeness has been attained. Some new minerals, *e.g.*, coronadite and morencite, which have been discovered in Arizona are described, and the results of the analyses of them are given.

A Primer on Explosives for Coal Miners. By Charles E. Munroe and Clarence Hall. Washington: Government Printing Office. 1909.

This bulletin has been published in the hope that it may lessen the loss of life and accidents due to the improper use of explosives by disseminating knowledge of their nature and the precautions which should be observed in handling, storing, and employing them. The authors put the dangers before their readers in very plain unequivocal language, and explain the proper methods of loading and firing charges of explosives, and the nature and use of fuses, squibs, detonators, &c. A good deal of practical information on mining coal with explosives is included, and the authors may be congratulated upon having produced a book which explains a highly technical subject in non-technical language which can readily be understood by mine-managers and foremen.

Metingen betreffende de toestandsvergelijking van Argon. ("Measurements Relating to the Equation of Condition for Argon"). By C. A. CROMMELIN. Leiden: Eduard Ijdo. 1910.

THIS book contains a critical study of the application of van der Waals' equation to argon, and the author has thoroughly summarised the literature of the subject. The preparation and purification of argon for the purposes of taking the observations are carefully explained in detail, and a complete list is given of the isotherms from -150 to 20°. Its vapour tension and critical temperature and pressure are also discussed, and the critical density is calculated. The book contains plates showing the apparatus used in the preparation of the gas and also the sotherms, and gives a useful summary of the determination of the physical constants of argon.

CORRESPONDENCE.

THE MOLECULAR VOLUMES OF SOLIDS.

To the Editor of the Chemical News.

SIR,—In my paper on the above subject (CHEMICAL NEWS, 1910, ci., 172), I noted on theoretical grounds that telluric acid was quite exceptional in its molecular volume. My forecast has now been practically confirmed by H. B. Baker and G. H. J. Adlam (*Proc. Chem. Soc.*, 1911, xxvii., 17), who find that telluric acid always contains an excess of water even when dried for six months in a vacuum. This, of course, would lower its density and therefore throw up its molecular volume so that it refused to conform to the hypothesis I submitted.—I am, &c.,

H. H. STEPHENSON.

CHEMICAL QUALIFICATIONS.

To the Editor of the Chemical News.

SIR,—I should like to point out to employers of analytical chemists that the examinations for the degrees of B.Sc. in chemistry and metallurgy of the various Universities, also the higher examinations of the Board of Education in chemistry and metallurgy, are evidence of high qualifications and training in chemistry and metallurgy.

The Board of Education examinations and the degrees of the University of London are the only examinations open to students of evening classes at the Technical Schools. The higher Board of Education examinations in chemistry and metallurgy, both theory and practical, are essentially practical and a thorough test of efficiency; personally, I should advise all students to take them in addition to any other examinations they may be preparing for. Many employers take far more notice of these certificates than degrees and similar examinations.

I would point out that membership of a scientific society does not confer any right to the title "professional chemist," "duly qualified chemist," or any similar title; all it confers is a right to use certain initials, which, in recent years, have been mainly given for passing examinations. I do not say anything against these examinations; my experience with assistants who have passed them has been very satisfactory. The point I wish to emphasise is that there are other highly qualifying examinations which do not carry any right to use any initials.

In consequence of the continued hostility shown to evening classes in certain quarters it appears to be necessary to point out to gentlemen holding official positions as teachers in evening classes at Technical Schools, that it is their duty to the ratepayers who employ them, and to the students who have to rely upon their teaching, to do their best to find positions in laboratories and works for their students, and to use all means in their power to press forward the fact that the examinations they prepare students for are qualifications; and it is no part of their duty to support, in any way, any society which has an "Appointments Register" unless that society admits the evening students they teach on the same terms as day students.—I am, &c.,

ERNEST A. LEWIS.

OBITUARY.

PROFESSOR JOHN ATTFIELD, F.R.S.

WITH regret we record the death on Saturday last of Professor Attfield, at the age of seventy-five. The deceased had occupied the Professorship of Chemistry to the Pharmaceutical Society for thirty-four years. Next week we hope to give an account of some of the work performed by Prof. Attfield in the domain of Pharmacy and Chemistry, and of researches to which he had devoted considerable attention.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliı., No. 4, January 25, 1911.

Transformation of $\alpha\beta$-Phenyl Pentenic Acid into its $\gamma\delta$-Isomer.—J. Bougault.—Fittig has shown that $\alpha\beta$-pentenic acids are readily transformed into their $\beta\gamma$-isomers by heating with alkalis, but the author finds that $\alpha\beta$-phenyl pentenic acid yields no $\beta\gamma$-acid but the $\gamma\delta$-acid $C_6H_5—CH=CH—CH_2—CH_2—CO_2H$. The reaction appears to be complex, and some β-oxy acid is formed, as well as an acid liquid which has not been identified.

Acetylenic Pinacone.—Georges Dupont.—Acetylenic pinacone behaves towards hydracids like the corresponding saturated pinacone or like two molecules of tertiary alcohol, at any rate at low temperatures. Towards dehydrating agents it shows more resemblance to malonic pinacone, giving an ethylenic alcohol with dehydration of a methyl chain. But the dehydration is more complete, and the molecule of glycol behaves like two molecules of tertiary alcohol.

Complete Destruction of Organic Matter for the Detection of Inorganic Poisons.—Pierre Breteau.—To 300 grms. of the organic substance 300 cc. of sulphuric acid ($D=1{\cdot}84$) are added, and nitrous vapours are passed into the heated mixture. The organic matter gradually dissolves and chars, and finally the black liquid becomes quite clear and straw-coloured. It may then be concentrated in a platinum dish and examined for the presence of mineral poisons.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Royal Society of Arts, 8. "Applications of Electric Heating," by Prof. J. A. Fleming, F.R.S.

TUESDAY, 28th.—Royal Institution, 3. "Explorations of Ancient Desert Sites in Central Asia," by M. Aurel Stein.

WEDNESDAY, 29th.—Royal Society of Arts, 8. "Art Education in Jewellery, Goldsmithing, and Allied Trades," by G. B. Heming.

THURSDAY, 30th.—Royal Institution, 3. "Surface Combustion and its Industrial Applications," by Prof. W. A. Bone, F.R.S.

— Royal Society. "Chemical Dynamics of Serum Reactions," by Capt A. G. McKendrick. "Preliminary Note on a Method of Measuring Colour Sensations by Intermittent Light, with Description of an Unfinished Apparatus for the Purpose," by Dr. G. J. Burch. "Variation and Adaptation in Bacteria, illustrated by Observations upon Streptococci, with special reference to the Value of Fermentation Tests as applied to these Organisms," by E. W. A. Walker. "Interrelations of Genetic Factors," by W. Bateson and R. C. Punnett. "Case of Gametic Coupling in Pisum," by P. de Vilmorin and W. Bateson. "Gametic Coupling and Repulsion in *Primula sinensis*," by R. P. Gregory.

FRIDAY 31st.—Royal Institution, 9. "Travelling at High Speeds on the Surface of the Earth and Above it," by Prof. H. S. Hele-Shaw.

SATURDAY, April 1st.—Royal Institution, 3. "Radiant Energy and Matter," by Prof. Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. CIII., No. 2679.

STUDIES OF THE PROCESSES OPERATIVE IN SOLUTIONS.

XIII.—The Depression of the Hydrolytic Activity of Acids by Paraffinoid Alcohols and Acids.

By HENRY E. ARMSTRONG and F. P. WORLEY.

It is known that, as a rule, alcohol retards chemical change, although there are cases in which it has an accelerating effect. In the first of these communications, it was shown that ethylic alcohol has a marked effect in retarding the hydrolysis of cane sugar, even when only a single molecular proportion is added to a weight-normal solution of chlorhydric acid and sugar, the value of *K* falling from 510 to 467. Caldwell, in discussing this result, has pointed out that :—

"Alcohol may be pictured as acting in at least three ways :—(1) Mechanically, by its interposition between the acting substances ; (2) as exercising a concentrating effect, such as the sugars exercise by combining with water ; (3) as entering into association with the active agent, viz., hydrogen chloride, forming an 'alcoholate.' Of these, (1) and (3) would be unfavourable, whilst (2) would accelerate the change. There is every reason to suppose that all three influences are operative and that the concentrating effect of alcohol is more than counterbalanced by the extent to which it interferes mechanically and probably, more especially, by the formation of an alcoholate."

Later observations lead us to think that cause (1) rather than cause (3) is mainly operative in retarding change. The experiments carried out by one of us in conjunction with Dr. Eyre, of which an account was given to the Royal Society of London on June 24th, 1909 (*Proc. Roy. Soc.*, 1910, A, lxxxiv., 123), show that the diminution in solubility of sodium chloride and other haloids effected by alcohols varies, in the case of the alcohols of the methylic series, as the molecular weight increases, propylic alcohol being a more effective precipitant than ethylic and methylic, alcohol, and the former alcohol more effective than the latter.

Subsequent observations show that *iso*butylic is considerably more effective than propylic alcohol.

The same relationship is apparent on contrasting the effect alcohols have in reducing the molecular electrical conductivity of solutions of salts, a subject discussed in No. XVII of these communications.

We have learnt recently from Professor Adrian J. Brown that observations on the rate at which water enters into the barley grain from alcoholic solutions also show that the rate of entry of water together with the alcohol is more rapid in the order given, in the case of propylic, butylic and amylic alcohols, than in that of the lower homologues, except that methylic appears to be more active than ethylic alcohol.

Similar observations made by one of us and E. F. Armstrong on the rate at which the alcohols gain entry into leaves such as those of the cherry-laurel (*Prunus laurocerasus*) and the Japanese laurel (*Aucuba japonica*) show that the higher alcohols of the ethylic series are the more active. We have obtained evidence with these alcohols also, in quite another way, of an increase in activity as the series is ascended.

In all these cases, as no acid is present, the effect would seem to be of a "mechanical" order ; it cannot come under Caldwell's case (3).

Caldwell has shown that acetic acid has a slight positive or "concentrating" effect equivalent to the withdrawal of one from about 55 molecules of water, the value of *K* being raised from 510 to 521 by the addition of a molecular proportion of the acid. Like the alcohols, the acids of the acetic series influence the rate of entry of water into the barley grain, water entering more rapidly with the acid from solutions of the higher acids ; moreover, J. Loeb has found this relationship to hold good in the case of entry of acids into the echinoderm egg, as shown by the rate at which the eggs begin to develop.

It is highly remarkable in the case of the monhydric alcohols and monobasic acids, that activity is greatest, however tested, in the case of the compounds which are least soluble in water and that their activity is in some way (inversely) proportional to their solubility.

In order to determine the effect, in several cases of chemical change, of paraffinoid alcohols and acids, we have subjected cane sugar to the action of chlorhydric acid in presence of the various substances. In all cases, the solution used contained a single molecular proportion of hydrogen chloride and of the added substance, together with a quarter of a molecular proportion of sugar and either 50 or 80 molecular proportions of water. Hydrolysis was effected at 25°.

The results with ethylic alcohol and acetic acid are in agreement with Caldwell's earlier observations. As we anticipated would be the case, methylic alcohol is less but propylic more effective than ethylic alcohol ; butyric acid, in like manner, is more effective than acetic acid, in that it has a distinct depressant influence whilst acetic acid has a slight accelerating influence.

The values arrived at are as follows :—

Effect of Alcohols of the Ethylic Series and of Acids of the Acetic Series on Hydrolytic Activity.

Added substance, 1 molecular proportion.	50 molecular proportions of water. *K*.	80 molecular proportions of water. *K*.
HCl (alone)	580	303·5
$CH_3(OH)$	549	295
$C_2H_5(OH)$	534	290
$C_3H_7(OH)$	518	285
$CH_3(CO_2H)$	600	310
$C_3H_7(CO_2H)$	570	301
NaCl	833	388
$NaCl + C_3H_7(OH)$ ..		358

The influence exercised by acetic acid would seem to be a true concentrating effect, as the specific hydrolytic activity of the acid is too slight to account for the effect it produces.

It is to be supposed that the changing system is one composed of the "hydrated" hydrolyte and the "hydrated" catalyst (the acid) and that such complex systems are formed reversibly. If hydrolysis take place only in a certain proportion of the systems, any interference with the formation of the systems would reduce the rate at which hydrolysis is effected. But a variety of influences must be at work, as glycerol is considerably less active than ethylic alcohol in retarding change, although a larger molecule ; moreover, the glucoses are apparently without influence. The nature of the influence exercised will be more fully discussed in a later communication.

(Note.—The communication of which this is the immediate sequel appears in the March issue of the *Journal of the Chemical Society*, together with Nos. 14 and 15. The withdrawal of the articles now published in this journal —this being the fourth—was rendered necessary solely by the refusal of my request that I might be allowed to qualify a noun by an adjective—the noun alcohol by adjectives such as methylic, etc. I have resented such arbitrary action on literary grounds as well as because it is an interference with the proper liberty of speech which must, I contend, be permitted to authors of communications to scientific societies. I may quote the following classic telegram received from the Editor on February 10th as an illustration of the condition to which we are reduced :—

"In view Committees letter cannot accept Methanol etc. for methyl alcohol etc. must have your acceptance letter before publishing papers further reference Committee delays publication till March."

This to a Fellow of over forty years standing who was an active member of the Geneva Conference on Nomenclature! The mind being occupied in various directions and oppressed by difficulties, in rendering an account of our work it is never easy to give correct expression to our thoughts; we are too often, through carelessness, guilty of using incorrect expressions—that an attempt should be made to impose their use is intolerable.—H. E. A.).

THE VOLUMETRIC DETERMINATION OF URANIUM.

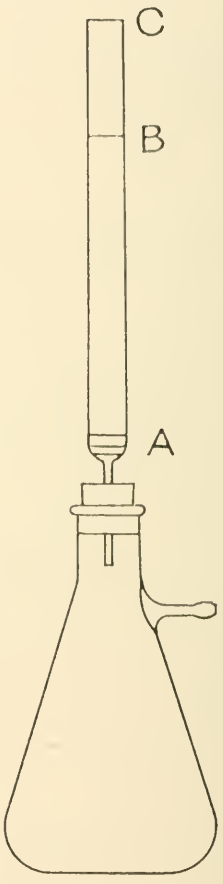
By F. IBBOTSON, B.Sc., and S. G. CLARK.

OF the few volumetric methods for the determination of uranium, the principal one depends upon the reduction of a uranyl solution, followed by a titration of the reduced solution with potassium permanganate. The reducing agent commonly employed is zinc, which is added in very large excess to the uranyl solution containing much free sulphuric acid, and the completion of the reduction is determined either by the thorough solution of the zinc, or by the time empirically specified for the reduction of a definite amount of uranium, or by the change of colour from the yellow of uranyl solutions to what is described by some observers as a clear chromium green and by others as the green of nickel solutions. The reductions are usually conducted in hot solutions, and in all cases it seems to be necessary that precautions should be taken to prevent the atmospheric oxidation of the reduced solution during the subsequent manipulations. In a paper on "The Quantitative Separation and Determination of Uranium" (*Journ. Am. Chem. Soc.*, xxiii., No. 10; and CHEMICAL NEWS, lxxxiv., 224 *et seq.*), Kern, for example, used about 50 grms. of pure zinc in lumps for the reduction of from 0·1 to 0·2 grm. of uranium. The reduction was carried on at the boiling-point of the solution, every four to five parts by volume of which contained one part of sulphuric acid. The zinc was allowed to dissolve completely, and the solution was then rapidly transferred to a flask containing a grm. of sodium carbonate, and titrated at once. Kern observes that "the time required for the reduction of about 0·1 grm. of uranium by zinc is about one hour, for about 0·2 grm. not less than one and a-half hours. The uranyl sulphate solution, at first yellow in colour, changes to light green, and finally to green with bluish tinge, having the appearance of a dilute solution of nickel chloride, which colour it retains even though the reduction be continued for as long as four hours."

Much time is saved as a rule if reductions with nascent hydrogen are conducted in a Jones reductor, which has become an almost indispensable tool in the equipment of analytical laboratories, more especially of those concerned primarily with the analysis of steel and steel-making alloys. The Jones reductor consists essentially of a column of finely divided amalgamated zinc contained in a tube through which the solution to be reduced is allowed to filter under suction into a flask. Blair ("The Chemical Analysis of Iron") makes use of the reductor for the determination of phosphorus in steel, and it has been applied to the determination of vanadic acid by Gooch and Edgar (*Am. Journ. Sci.*, xxv., 233), by Edgar to the determination of molybdic and vanadic acids (*Am. Journ. Sci.*, xxv., 332), and also to the determination of vanadium and iron in the presence of one another (*Am. Journ. Sci.*, xxvi.).

For the reduction of uranium solutions Kern recommends a longer reductor than usual, and makes use of a column of 20-mesh zinc about 45 cm. long, contained in a burette—the ordinary length is about 30 cm. He finds that "the most satisfactory results were obtained when the ratio of free sulphuric acid (sp. gr. 1·84) to total solution was not less than 1 to 6 nor more than 1 to 5. When the solutions contained more acid than the ratio of 1 to 5, the zinc sulphate which formed did not go into solution, and prevented the ready passage of the solution through the reductor. When the acid was present in amounts less than the ratio of 1 to 7, the reduction of the solution was incomplete, due to too slow action of the acid on the zinc. The reduction was complete in all cases when the ratio of free sulphuric acid to total solution was within the limits of 1 to 6 and 1 to 5."

An extensive experience with the Jones reductor led us to adopt a simpler form of it for the reduction of uranium solutions. It is shown in the accompanying figure. The



length A C is about 22 cm., and A B, which is occupied by the zinc, is 15 cm.—the diameter is 2 cm. A filter-plate covered with a layer of ignited asbestos fibre is placed at A. The side opening of the flask is connected to an ordinary bottle for supplying the small amount of aspiration necessary.

The zinc was amalgamated by shaking it in a flask with a solution of mercuric sulphate in 2½ per cent sulphuric acid, the usual proportion being 1 grm. of metallic mercury for every 100 grms. of zinc. After washing several times with 2½ per cent sulphuric acid, and finally with water, the zinc was transferred to the reductor-tube and kept permanently covered, when not in use, with water. About 120 grms. of 20 to 30-mesh zinc were required.

In all the reductions made by us, 100 cc. of sulphuric acid of the strength specified in the appended results were first passed through the column of zinc, next the uranyl solution acidified to the same extent, then 100 cc. more

acid, and finally 100 cc. of water. A blank determination on the reagents never showed more than 0·1 cc. of N/20 permanganate in the titration. *Cold* solutions were used throughout.

The uranyl solution was prepared from Kahlbaum's acetate, and was carefully assayed gravimetrically by precipitation as phosphate; 50 cc. of the solution contained 0·2566 grm. of the metal, which requires theoretically a consumption of 42·77 cc. of N/20 permanganate in the titration of the reduced solution.

The following figures are selected from a very large number of results obtained :—

Acid strength (per cent).	Permanganate (cc.).	
1	43·4	43·2
2½	43·3	43·6
5	43·9	45·8
10	44·9	44·3

In each of these tests the colour of the reduced solution was certainly not that of pure uranous solutions, but *brownish* green, and the greater the degree of reduction the greater the suppression of the clear green of pure uranous solutions.

After aspirating a current of air through the reduced solutions for a minute or so, the brown tint was completely dispelled, and, on titrating, the lowest reading of the permanganate was 42·7 cc. and the highest 42·9, representing 0·2562 and 0·2574 grm. uranium respectively. The correct reading 42·8 cc. was given in the majority of the large number of tests made.

A further set of tests, using a 2 per cent amalgam, gave the following results :—

Acid strength (per cent).	N/20 $KMnO_4$ used (cc.). Before aspiration of air.	After aspiration of air.
1	43·3	42·8
2½	44·6	42·8
5	45·5	42·8
10	45·9	42·9

It is evident from the above figures that the reduction of cold uranyl solutions to the uranous condition is more than completed during the short time (about five minutes) occupied by their passage through the column of zinc, but the results show varying degrees of reduction, no one of which corresponds to any definite chemical composition. It is further evident that cold uranous solutions are much more stable than is generally supposed, since the aspiration of air which in several experiments was continued at a brisk rate for twenty minutes, did not result in a measurable amount of oxidation. An attempt was made to carry the reduction to the condition corresponding to the formula $U_2(SO_4)_3$, which would have involved 64·15 cc. of N/20-permanganate in the titration. This was done by first passing the solution through the short reductor as above, and then passing the reduced solution through a much longer reductor into a receiver containing an excess of ferric alum so as to eliminate atmospheric oxidation. The titration figure was 50·2 cc., from which it is seen that zinc in sulphuric acid solution will not effect the reduction to $U_2(SO_4)_3$, a conclusion also reached by Kern (*loc. cit.*).

As already stated, cold solutions were used in the above experiments, but when, instead of passing the uranyl solutions through a reductor, they were brought into contact with a large excess of amalgamated zinc in an open vessel and the *solutions were heated*, it was at once obvious that a very rapid reduction took place, even in solutions of 2½ per cent acid. In less than five minutes, that is, before the solutions reached boiling point, the change from yellow through the clear green to dark brown had taken place. After passing the hot solutions through a small filter to strain off tiny particles of zinc, and washing, the following extraordinary readings were obtained on titration with permanganate :—41·5 cc., 40·8, 41·1, 41·6, &c. Oxidation had thus taken place during the filtration and subsequent manipulations, a fact evidenced by the colour changes during the performance of these operations.

The stability of cold uranous solutions having been established, the only factor which could determine this oxidation was evidently the temperature of the solutions. A further set of reductions was therefore made by heating the solutions as before, and, when a strong brown colour was developed, the flasks were rapidly cooled to ordinary temperature. In every case, after filtering and washing, and aspirating air for a minute, or even after allowing the solution to remain exposed to the air for twenty minutes, the readings of the permanganate were 42·7 or 42·8 cc.

The volumetric determination of uranium can therefore be made in about fifteen minutes by the following process :—Pour the solution of uranyl sulphate containing from 2 to 5 per cent by volume of free sulphuric acid into a flask containing about 50 grms. of pure finely divided and amalgamated zinc (20 to 30-mesh) and heat until a dark brown colour is developed. Cool the flask rapidly under a stream of water, and then pour the cold solution through a small pulp-filter, wash with cold water, aspirate air for a minute through the filtrate, and titrate with permanganate.

The zinc may be used for a dozen determinations at least before it requires further amalgamation. The reduced solution can be poured through the filter without carrying more than a few particles of the metal with it.

Since uranyl solutions are not reduced by sulphurous acid, a mixture of ferric sulphate and uranyl sulphate can be assayed by first reducing the iron with sulphurous acid, titrating with permanganate, and then treating the titrated solution as above.

Metallurgical Department,
The University, Sheffield.

DETERMINATION OF TIN AND ANTIMONY IN SOFT SOLDER.

By J. H. GOODWIN.

The following details for the rapid volumetric determination of tin and antimony in soft solder are adapted from A. H. Lowe's method (*Journ. Am. Chem. Soc.*, xxix., 66).

Antimony.—On a counterpoised watch-glass weigh exactly 2 grms. of filings, which should be fine enough to pass a 30-mesh sieve. With a quill brush transfer the filings through a stemless funnel into a 300 cc. Jena Erlenmeyer flask. Add 5 grms. of $KHSO_4$ crystals and 10 cc. of sulphuric acid, specific gravity 1·8. By means of cork-lined tongs or test-tube holder manipulate the flask over a bare Bunsen flame until most of the free acid is expelled and no sulphur remains on the walls of the flask nor in the liquid. Do not attempt to take to dryness. Place the hot flask on a piece of asbestos. The tin is now all a stannic and the antimony all an antimonous salt. When the flask cools sufficiently add 25 cc. of cold water and 5 cc. of hydrochloric acid, specific gravity 1·2 (P. H. Walker and H. A. Whitman also use less hydrochloric acid than A. H. Low, *Journ. Indust. and Eng. Chem.*, i., 519). Manipulate over a free flame for half a minute to complete the solution of the tin and antimony salts and to expel any sulphuric dioxide. Cool the flask under running water. Add 100 cc. of cold water, and titrate rapidly with N/20 potassium permanganate. From the volume of the latter required to give the first pink colour calculate the per cent of antimony. Dry to constant weight some highest purity sodium oxalate, made according to Sorensen, and use this to standardise the N/20 potassium permanganate solution.

Tin.—Weigh exactly 0·2 grm. of the filings and transfer as before to a 300 cc. Jena Erlenmeyer flask. Add 5 cc. of 15 per cent sodium carbonate solution. Add 20 cc. of hot water. Add 25 cc. of hydrochloric acid, 1·2 specific

gravity. Add 1 drop of 5 per cent antimony chloride solution from a dropping bottle. This solution should be strongly acid with HCl. Close the flask with a 1-hole rubber stopper carrying a capillary U-tube of 1 mm. bore. The short arm of the U-tube should just reach through the stopper, while the long arm should almost reach the surface on which the flask stands. Place the flask on a hot plate where it will boil very slowly but not suck air back through the tube. The solder will dissolve in about fifteen minutes, leaving a small black precipitate of antimony. As soon as this occurs, and without interrupting the slow boiling, bring a test-tube of 15 per cent sodium carbonate solution under the U-tube. Carry to the sink and cool the flask under running water, allowing the carbonate solution to suck back into it. When cold, add 5 cc. of 15 per cent sodium carbonate solution and 5 cc. of cold fresh starch liquor, and titrate immediately with N/20 iodine solution. From the volume of the latter required to give the first deep blue colour calculate the per cent of tin. Standardise the N/20 iodine solution by titrating in the same way 0·1 grm. portions of filings made from a stick of Kahlbaum's highest purity tin.

This method can be used to advantage for soft solder containing 0 to 2 per cent of antimony, 30 to 60 per cent of tin, 40 to 70 per cent of lead, and not more than traces of any other metals. Duplicate determinations of tin and antimony can be made in one hour.—*Journal of Industrial and Engineering Chemistry*, iii., No. 1.

METHODS OF ANALYSIS AND TESTS OF FATS AND OILS SUGGESTED BY THE SPECIAL COMMITTEE OF COMMITTEE ON THE UNIFORMITY OF ANALYSIS OF FATS AND FATTY OILS.*

THESE methods are proposed tentatively with the object of inviting criticism and discussion).

1. *Moisture and Volatile Matter.*

Weighing out Sample.—By the application of gentle heat soften, but do not melt, the sample, and emulsify thoroughly by means of a mechanical egg beater (or other suitable device). Of the thoroughly emulsified sample weigh out for the standard methods from 5 to 20 grms. according to the method used from weighing bottle into a watch-glass or shallow glass dish whose sides are not more than 1 cm. high.

Standard Method No. 1, Moisture and Volatile Matter at 110° C.—A 5—10 grm. sample weighed out as above is heated in an oven held at a constant temperature of 110° C. until constant weight is attained. Constant weight is attained when successive weighing thirty minutes apart show a loss of not more than 0·05 per cent.

Standard Method No. 2, Moisture and Volatile Matter.—A 5—10 grm. sample weighed out as above is heated in a vacuum oven held at 50° C. under a pressure of not more than 30 mm. of mercury for four hours. (The tension of water vapour at 50° C. is 92 mm.).

Routine Method, Moisture and Volatile Matter.—The sample weighed out in a glass or aluminium beaker as above is heated on a heavy asbestos board over burner or hot plate, the sample at no time being allowed to reach a temperature greater than 130° C. During the heating the beaker is rotated gently on the board by hand to avoid sputtering or too rapid evolution of moisture. The proper length of time of heating is judged by absence of condensation on a cold watch-glass held over the beaker, by the absence of rising bubbles of steam, by the absence of foam, or by other signs known to the operator. Cool in desiccator and weigh. Report loss as moisture.

* American Chemical Society.

2. *Moisture.*

The term "moisture," as here used, refers to the chemical substance "water" physically incorporated in the fats and fatty oils.

Standard Method.—(Similar to that mentioned by Ubbelohde).

100 grms. of the sample are mixed with 100 cc. of xylene in a suitable distilling flask, and about 50 cc. slowly distilled off over a free flame. The distillate containing the water is collected in a tube 0·75 cm. diameter graduated in 1/10 cc., and the percentage of water read off directly from the volume of water contained in the tube. Correction is to be made for the solubility of water in xylene. Details to be supplied. (The boiling-point of xylene is 138° C.).

3. *Suspended Impurities.*

Definition.—Suspended impurities in fats and fatty oils are those non-fatty solid substances physically incorporated therewith and insoluble in hot petroleum ether, such as particles of wood, coal, fibres, and mineral matter. They are determined by the standard method given below.

Determination: Standard Method.—A sufficiently large sample to be representative should be weighed out and dried, or the residue from a moisture and volatile matter determination may be used. Usually from 5—20 grms. should be used. The sample is dried in a beaker over asbestos board, keeping the beaker in motion by hand to prevent sputtering. The sample is then dissolved in hot petroleum ether (boiling-point 50—70° C.) by gentle boiling on a water-bath, filtered on a Gooch crucible or porous crucible, washed thoroughly with a boiling petroleum ether (boiling-point 50—70° C.), dried to constant weight, and weighed.

4. *Free Fatty Acids.*

Preparing Neutral Alcohol.—Take commercial 95 per cent alcohol, add 50 grms. powdered caustic soda per litre, boil with reflux condenser for a period of six hours, allow to stand for twenty-four hours, and then distil. Alternate method.

Determination.—From 5—15 grms. of the sample are weighed into an Erlenmeyer flask (100 cc. capacity) and melted on the steam-bath, if solid at ordinary room temperature. Add 100 cc. of hot neutral alcohol. Titrate with N/2, N/4, or N/10 sodium hydrate, using phenolphthalein as indicator. Where the fat is known to have a mean molecular weight of 282 or thereabouts, that figure is to be used in calculating the percentage of free fatty acids. Report also the acid number: mgrms. KOH required to neutralise 1 grm. The percentage of free fatty acids is to be calculated on the basis of sample freed from moisture and volatile matter.

5. *Titre.*

Method Proposed by L. M. Tolman as follows (Bureau of Chemistry, *Bulletin* 107, revised):—"Weigh 75 grms. of fat into a metal dish, and saponify by using 60 cc. of 30 per cent sodium hydrate (36° Baumé caustic soda) and 75 cc. of 95 per cent by volume alcohol, or 120 cc. of water. Boil down to dryness, with constant stirring, to prevent scorching. This should be done over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a litre of boiling water, and if alcohol has been used boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent sulphuric acid (25° Baumé sulphuric acid) to free the fatty acids, and boil until they form a clear transparent layer. Collect the fatty acids in a small beaker, and place on the steam-bath until the water has settled, then decant them into a dry beaker, filter, using a hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titre and transfer to the titre-tube, which is 25 mm. in diameter and 100 mm. in length (1 by 4 inches) and made of glass about 1 mm. in thickness. This is

Placed in a 16 ounce salt-mouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2¾ × 6 inches), fitted with a cork which is perforated so as to hold the tube rigidly when in position. The thermometer, graduated to 0·1° C., is suspended so that it can be used as a stirrer, and the mass is stirred slowly until the mercury remains stationary for thirty seconds. The thermometer is then allowed to hang quietly with the bulb in the centre of the mass, and the rise of the mercury observed. The highest point to which it rises is taken as the titre of the fatty acids.

"The fatty acids are tested for complete saponification as follows:—Three cc. of the fatty acids are placed in a test-tube and 15 cc. of alcohol (95 per cent by volume) added. The mixture is brought to a boil and an equal volume of ammonia (0·96 sp. gr.) added. A clear solution should result, turbidity indicating unsaponified fat. The room temperature must be reported."

Proposed Exceptions.—The fat is to be saponified in an iron or porcelain dish, and fatty acids set free in porcelain, fatty acids to be dried twenty minutes at 105° C., instead of at 100° C.

6. *Unsaponifiable Matter.*

Definition. The non-fatty acid constituents of fats and fatty oils, soluble in petroleum ether (boiling-point 35° to 50° C.).

Determination.

Standard Wet Method.—Three grms. of the sample, free from moisture and volatile matter, are weighed into a 150 cc. flask, and a 30 per cent excess of strong colourless or nearly colourless alcoholic potash solution added. The contents are boiled for one hour under a reflux condenser, and then transferred to a stoppered 100 or 150 cc. cylinder and made up to 50 cc. with cold water. Add 30 cc. of re-distilled petroleum ether (boiling-point 35—50° C.), and agitate vigorously. Draw off the petroleum ether layer by means of slender glass syphon. Repeat this operation with five separate portions of petroleum ether. Place the 150 cc. of petroleum ether into a Squibb's pear-shaped separatory funnel (250 cc.), and wash three times with 20 cc. of 50 per cent alcohol. Pour the contents of the funnel into a tared flask, and distil off the greater part of the petroleum ether and complete the drying on a steam-bath and in an oven, the latter held below 105° C.

Standard Dry Method.—Approximately 5 grms. of fat or oil are weighed into a 200 cc. capacity Soxhlet or Erlenmeyer flask, and saponified with sufficient alcoholic sodium hydrate solution to give 50 per cent excess of sodium hydrate by boiling under a reflux condenser for half-an-hour to one hour or until saponification is complete. The solution is then transferred to a 4-inch porcelain evaporating dish (the flask being rinsed with hot alcohol) and dried on a water-bath. The drying is completed in the oven at 120° C. for one to two hours. Grind the dried soap in an agate mortar with 10—15 grms. granular anhydrous sodium carbonate, and place the whole in a 33 × 80 mm. S. and S. extraction thimble, using a fat-free plug of cotton to cover the charge. Place the thimble and contents in oven, and re-dry for one hour at 110—120° C. The extraction is made with re-distilled light petroleum ether boiling from 35—50° C. During the extraction if a Soxhlet or Knorr apparatus is used the open end of condenser must be protected against atmospheric moisture by a $CaCl_2$ tube. All connections of the apparatus must be tight. The extraction is allowed to proceed for about ten hours (if a Soxhlet apparatus is used at least 50 discharges). Transfer the extract to a weighed beaker, evaporate solvent on the water-bath and dry in an oven to constant weight. Test the extract by re-dissolving in light petroleum ether; a clear solution should be obtained if the determination has been properly carried out.

7. *Metallic Soaps.*

Definition.—The insoluble metallic soaps in the present sense are the fatty acid compounds of bases other than the alkalies. They are insoluble in water.

Determination.

Standard Method No. 1.—The filtrate from the suspended impurities determination (including the hot petroleum ether washings) is evaporated to a bulk of about 200 cc., and allowed to stand over night or twelve hours in a cool place (18—20° C.). It is then filtered from the separated insoluble metallic soaps on a Gooch crucible, washed with cold petroleum ether (boiling-point 35—50° C.), dried, and weighed.

Standard Method No. 2.—The filtrate from the suspended impurities determination is evaporated, burned, and ignited to constant weight. (*a*) The weight of the ash from metallic soaps thus obtained is to be reported as such. (*b*) Considering the ash to consist entirely of calcium oxide, it is to be calculated to normal soap, using 281 as molecular weight of fatty acid and reported as lime soap.—*Journal of Industrial and Engineering Chemistry*, iii., No. 1.

THE CHEMICAL SIGNIFICANCE OF CRYSTAL STRUCTURE.*

By Prof. WILLIAM J. POPE, M.A., F.R.S

LARGE numbers of chemical substances occur on the earth's surface as definite geometrical forms bounded by plane faces; these polyhedral shapes are called crystals. Inspection of the crystal forms assumed by mineral substances shows that, roughly speaking, each crystalline substance affects some specific geometrical shape which is characteristic for the material; further that, whilst crystals of any particular mineral attain vastly different dimensions and are bounded by planes which vary greatly in relative area, one geometrical feature remains constant. The angles between corresponding pairs of faces on any two crystals of the same substance are the same, notwithstanding the existence of difference in size, or in relative face magnitude between the two crystals. The constancy of interfacial angle amongst crystals of the same substance is a law of nature, and has been amply demonstrated by the very careful crystallographic measurements made by Tutton during the last twenty years.

It is, however, not essential to study mineral substances alone in order to obtain a knowledge of the laws governing crystal growth. Great numbers of laboratory products can be caused to crystallise by condensation from some fluid condition; thus, the crystals of various alums exhibited were obtained by slow evaporation of aqueous solutions of these salts.

The examination of a crystal shows that many of its physical properties differ according to the direction in the crystal in which the property is determined; the hardness of crystals, the speed at which light travels through them, and many other properties, are commonly dependent on the direction in which the material is examined.

The dependence of crystal properties on direction indicates the most essential feature of the crystal to be a definite and orderly arrangement of its ultimate particles; this arrangement is referred to as the crystal structure. Further evidence that crystals possess an arranged structure is furnished by the observation that crystallisation is not necessarily a spontaneous process. Thus, on melting benzophenone and rapidly cooling the clear molten mass, the liquid state is retained for many hours at a temperature far below the normal melting point of the compound. But on inoculating the liquid with a trace of crystalline benzophenone crystallisation immediately commences and rapidly becomes complete. The introduction of a small particle of crystalline or arranged material into the liquid mass provides a nucleus upon which the molecules are able to deposit themselves in a similar crystalline arrangement; the process thus started quickly becomes propagated throughout

* A Discourse delivered at the Royal Institution, April 15th, 1910.

the entire mass. The lack of spontaneity in the process of crystallisation leads occasionally to quite unexpected results. Thus, tetrahydroquinaldine has been known for many years, and has been prepared by numbers of chemists. It has always been obtained as a liquid, and has never been supposed capable of existing in the crystalline state at ordinary temperatures; even when cooled in liquid air it merely becomes a thick resin, and does not crystallise. But on dissolving a few drops of it in a little light petroleum and cooling the solution thus obtained in liquid air, the tetrahydroquinaldine crystallises out; on transferring a trace of the crystalline material obtained to the liquid substance at the ordinary temperature, the liquid mass is seen to immediately crystallise. This well-known substance, hitherto known only in the liquid state at ordinary temperatures, really exists in a more stable condition as a crystalline solid.

Many substances are capable of crystallising in two or more distinct crystalline forms of which one is, in general the more stable at any particular temperature. The physical properties of the several crystalline modifications of any one substance are quite distinct and characteristic for the particular crystalline form and, in many instances, even the colours of the several modifications are different. An example of this is afforded by pouring boiling water into a beaker coated with cuprous mercuric iodide; the brilliant scarlet crystalline form stable at ordinary temperatures, when heated in this way, becomes converted into another crystalline modification which is nearly black. The change is a reversible one, and the differences between the properties of the two crystalline modifications are to be attributed to differences in the mode of arrangement of the molecules in the two cases; the two modifications, in fact, possess different crystalline structures.

Although vast numbers of observations, such as the preceding, lead to the conclusion that crystals are arranged structures, it is not essential that the crystal should be a solid substance; during recent years large numbers of crystalline liquids have been discovered. On allowing melted cholesteryl chloride to cool rapidly a brilliant display of interference colours is seen, owing to the particles of the substance assuming crystalline or orderly arrangement whilst still retaining the liquid condition.

Having very briefly reviewed some of the many reasons for concluding that crystals are structured edifices, the nature of the architecture which they exhibit may now be considered. All the properties of crystalline solids harmonise with one simple assumption as to the manner in which the parts of the structure are arranged; this assumption is that the structure is a geometrically "homogeneous" one, that is, a structure the parts of which are uniformly repeated throughout, corresponding points having a similar environment everywhere within the edifice. The assumption of geometrical homogeneity as the characteristic of crystalline solids leads at once to the great problem solved by the crystallographers of the nineteenth century. This consisted in the inquiry as to how many types of homogeneous arrangement of points in space are possible, to the study of those types and to their identification, in symmetry and other respects, with the known systems into which crystalline solids fall. This work was commenced by the German crystallographer Frankenheim in 1830, and completed by the English geometrician Barlow in 1894. Briefly stated, the final conclusion has been attained that 230 geometrically homogeneous modes exist of distributing material, or points representing material throughout space, and that these 230 homogeneous types of structure, the so-called homogeneous "point-systems," fall into the 32 types of symmetry exhibited by crystalline solids. Models of a number of homogeneous point systems illustrating some of these types are exhibited.

It is, however, obvious that the limitation of the possibilities of solid crystalline arrangement to 230 types marks but one stage in the determination of the nature of crystal structure, and throws no direct light on the relation between crystal structure and chemical constitution. Although by the end of the nineteenth century we had learnt that corresponding points of the units of crystalline structures form homogeneous point-systems, the great problem still remained of determining what are the entities which become homogeneously arranged, for what reason they become so arranged, and in what way the conclusions drawn by modern chemistry are reflected in crystal structure. This problem was a legacy to the twentieth century, and it now remains to indicate briefly the extent to which it has been solved and the results of chemical importance which have accrued during its investigation.

The problem may be most easily visualised in connection with some comparatively simple case, that, for instance, presented by the crystalline forms assumed by the elements themselves. It is generally admitted that an elementary substance consists of identical atoms, each of which acts as a centre of operation of attractive and repulsive forces. In a solid crystalline structure the atoms are obviously not free to travel through the mass, each, if not indeed fixed to a particular spot, being retained within a certain minute domain; each of these domains must be regarded as possessing a centre which marks the mean position of the atom.

The crystalline condition of an element may consequently be defined as one of equilibrium between forces of attraction and repulsion emanating from or referable to a flock of points homogeneously arranged in space, that is to say, of points of a homogeneous point-system. Under these conditions, the space occupied by a crystalline element, a homogeneous assemblage of identically similar atoms, may be partitioned into identically similar cells in such a manner that the boundaries of a single cell shall enclose the entire domain throughout which a particular atom exercises predominant influence. Since it is postulated that every point in the space is subject to the dominating influence of some next neighbouring atomic centre, it follows that the cells fit together so as to occupy the whole available space without interstices. Nothing is here said about the shape of the cells; but since, in the case of an elementary substance, the atomic centres are all alike, so too will be the cells. Before proceeding to discuss the actual shapes of the cells referred to, it will be convenient to illustrate more graphically the mode of treating the problem which is here introduced with the aid of a particular point-system connected with the crystalline structure of elementary substances.

The point-system in question may be derived in the following manner. Space is first partitioned into cubes by three sets of parallel planes at right-angles to one another (Fig. 1); a point is then placed at each cube corner and at the centre of each cube face. The cubes of the partitioning, having served their purpose, may now be removed, leaving one of the 230 types of homogeneous point-systems (Fig. 2). Imagine next that each point of the system expands uniformly in all directions until it touches its neighbours a system of spheres packed together in contact is thus obtained (Fig. 3), and, on examination, it is found that no way exists of packing these equal spheres more closely together than the one thus derived. The system is therefore termed the cubic closest-packed assemblage of equal spheres and, being derived in the manner described, still retains the high symmetry of the cube; the fragment shown, in fact, outlines a cube. Three directions at right angles in it, those which are parallel to the three cube edges, are seen to be identical in kind; this identity in kind in the three rectangular directions, a, b, and c, is conveniently expressed by the ratio, $a : b : c = 1 : 1 : 1$.

On removing spheres from one corner of the cubic closest-packed assemblage of equal spheres a close triangularly arranged layer is disclosed, and, by similarly treating each corner of the fragment of assemblage, the cube outline gives place to one of octahedral form. The assemblage is now seen to be built up by the superposition of the disclosed triangularly arranged layers, the hollows in one layer serving to accommodate the projecting parts of the spheres in adjacent layers. When this operation is per

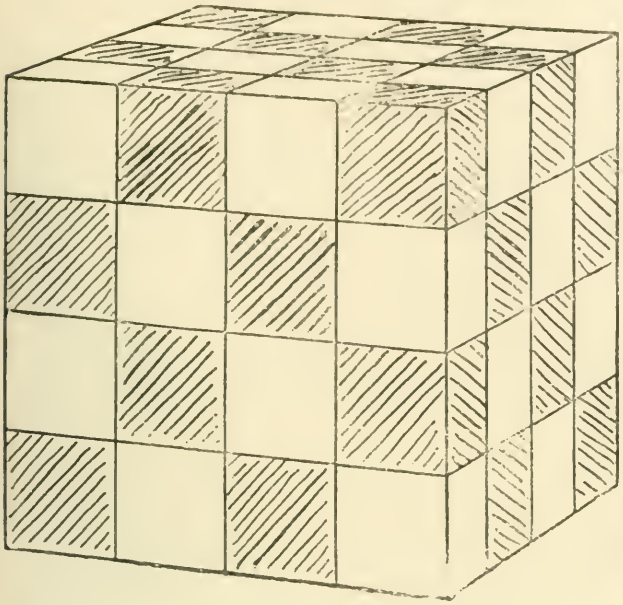


Fig. 1.

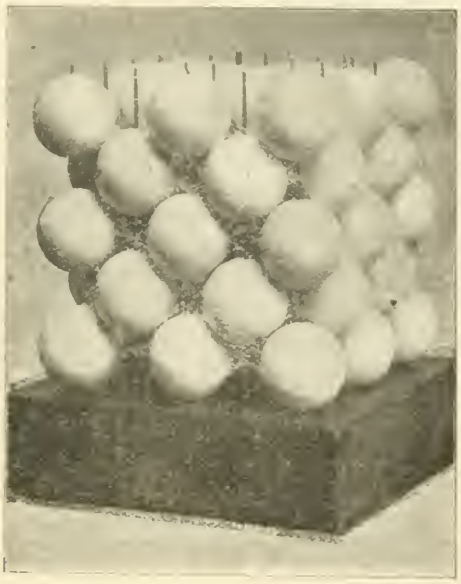


Fig. 3.

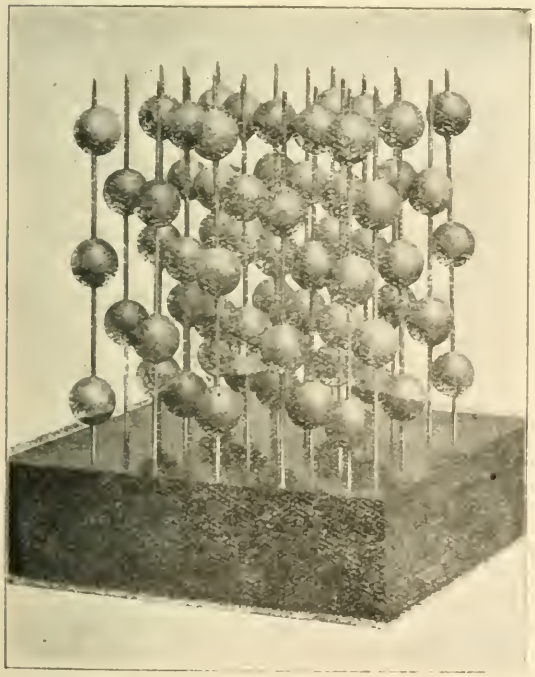


Fig. 2.

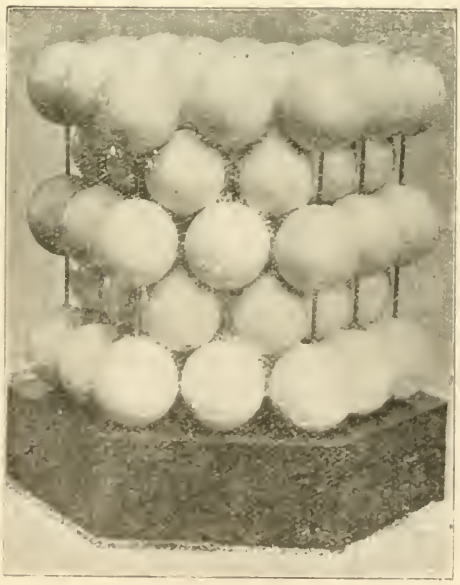


Fig. 4.

formed it is perceived, however, that two ways of stacking the layers homogeneously are possible, The first of these, in which the fourth layer lies immediately over the first, the fifth over the second, and so on, yields the cubic closest-packed assemblage. The alternative mode of stacking, in which the third layer lies immediately over the first, the fourth over the second, and so on, exhibits the same closeness of packing as the first, but possesses the symmetry of the hexagonal crystal system; it is accordingly termed the hexagonal closest-packed assemblage of equal spheres (Fig. 4). Examination of the hexagonal assemblage shows that the horizontal directions, in the planes of the layers, are not identical in kind with vertical directions, perpendicular to the planes of the layers.

Corresponding dimensions in these two directions, a and c, are in the ratio of

$$a : c = 1 : \sqrt{(\tfrac{2}{3})} = 1 : 0{\cdot}8165.$$

The final step in the treatment of the closest-packed assemblages of equal spheres consists in converting them into the corresponding assemblages of cells fitting together without interstices which have been already mentioned; it may be carried out in these, and in all other cases, by causing the component spheres to expand uniformly in all directions until expansion is checked by contact with the expanding parts of neighbouring spheres. The cubic closest-packed assemblage then becomes a stack of twelve-sided polyhedra, rhombic dodecahedra, which are so fitted together as to fill space without interstices. It is now seen that the even rate of expansion from each point of the original point-system which gives rise to the closely packed stack of rhombic dodecahedra, symbolises an even radiation in all directions of the forces of which the atom is the centre of emanation. On applying the same operation of expansion to the spheres present in hexagonal closest-packing, each becomes converted into a dodecahedron, although of symmetry different from that of the rhombic dodecahedron. In each of the two cases the system exhibits the important property that, with a given density of distribution of the centres, a maximum distance prevails between nearest centres; these two systems thus represent the equilibrium arrangements of the postulated forces of repulsion exerted between near centres, the repulsions between more distant ones being neglected.

It will be sufficiently evident from what has been said that the function of the spherical surfaces in the closest-packed assemblages of spheres, as representing crystal structures, is merely a geometrical one; these surfaces are employed only as so much scaffolding by the aid of which may be derived arrangements exhibiting a maximum number of equal distances between neighbouring centres, and no physical distinction is to be made between portions of space lying within the spheres and portions forming part of the interstices between them. Insistance on this point is necessary, because many investigators have made use, quite illegitimately, of spheres for the representation of atomic domains, piling the spheres together in what they have termed open packing; this term seems to imply that some physical difference can subsist between the portions of space lying within the spheres and those lying without. The one kind of space is apparently regarded as susceptible to atomic influence in some sense not exhibited by the other. To state this view in any definite manner probably suffices to demonstrate its superficiality; the question of ascertaining what proportion of the total space is available for atomic occupation by the use of assemblages of spheres does not arise because the spheres used are solely the geometrical instruments for producing equality amongst the atomic distances, and so determining the prevailing equilibrium conditions.

So far as the enquiry has been carried, it would seem that the elements should crystallise either in the cubic or the hexagonal system, and that in the latter case corresponding dimensions in the horizontal and vertical directions should be in the ratio of $a : c = 1 : 0{\cdot}8165$. The facts are summarised in Table I.

Of the elements which have been crystallographically examined, 50 per cent are cubic; their crystal structure is simulated by the cubic closest-packed assemblage of equal spheres. Another 35 per cent belong to the hexagonal system, and that these are correctly represented by the hexagonal closest-packed assemblage of equal spheres is indicated by the fact that for the hexagonal elements the ratio of corresponding dimensions in the horizonal and vertical directions approximate to the value $a : c = 1 : 0{\cdot}8165$, deduced for the model assemblage.

The task of accounting for the 15 per cent of the crystalline elements which have been examined and found to crystallise in systems other than the cubic or hexagonal still remains. A little inspection shows that the crystal

TABLE I.—*Relation between Crystal Form and Molecular Complexity.*

Crystal system.	Elements.	Number of atoms in molecules of compound inorganic substances. 2.	3.	4.	5.	More than 5.	Organic compounds
Cubic	50	68·5	42	5	12	5·8	2·5
Hexagonal . ..	35	19·5	11	35	38	14·6	4·0
Tetragonal . ..	5	4·5	19	5	6	7	5·0
Orthorhombic ..	5	3·0	23·5	50	36	27·3	34·0
Monosymmetric	5	4·5	3	5	6	37·3	47·5
Anorthic	0	0	1·5	0	2	8	7·0
Number of cases summarised in each vertical column	40	67	63	20	50	673	585

(The proportion of substances crystallising in each system is stated above as a percentage).

forms of these elements in every case approach very closely to one or other of the two of highest symmetry, namely, the cubic or the hexagonal; one example of this will now suffice. The values of corresponding dimensions in three directions in space for the monosymmetric form of the element sulphur are given by the axial ratios $a : b : c$ $0{\cdot}9958 : 1 : 0{\cdot}9998$, $\beta = 95° 46'$. The slight departure of these dimensions from the corresponding values for the cubic closest-packed assemblage, in which $a : b : c = 1 : 1 : 1$, $\beta = 90°$, at once suggests that the monosymmetric modification of sulphur is derived from the latter assemblage by some minute distortion. Such a distortion indicates a very trifling departure from uniformity in the influence exerted in different directions from each atomic centre, and may either arise from some want of symmetry in the individual atoms, or in a reduction of the symmetry caused by some grouping of the atoms; two or more atoms might thus be more closely connected in some way with one another than with other next neighbouring atoms.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 9th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Absorption Spectra of Lithium and Cæsium.*" By Prof. P. V. BEVAN.

This paper gives an account of the continuation of work done on the absorption spectra of vapours of the alkali metals. Difficulty was found in obtaining tubes which were not acted on by lithium vapour, and this difficulty was never completely surmounted. By the use, however, of considerable quantity of lithium in a steel tube the absorption spectrum was obtained, and twenty-seven lines of the principal series were observed. The measurements for the whole series are given in the paper, the lines from the tenth to the twenty-seventh being new. The paper further gives measurements of wave-lengths for the similar lines for cæsium. The series has been extended to include twenty-four lines, and re-measurements were made as there was pointed out by Prof. Hicks some probable errors in former determinations. The two series for lithium and cæsium are compared with the formulæ suggested by Hicks, and it is found that the agreement of calculated and observed wave-lengths is exceedingly good, a slight change in one of the constants for cæsium being indicated.

"*Dispersion in Vapours of the Alkali Metals.*" By Prof. P. V. Bevan.

This paper gives an account of measurements of the dispersion in rubidium and sodium vapours. The work is of the same character as that on the dispersion in potassium vapour described in the *Proceedings of the Royal Society*, 1910, A, lxxxiv. Dispersion curves for the rubidium vapour were obtained for the region of wave-lengths 6000 to 3000. Anomalous dispersion effects were observable at the first eight members of the principal series lines. These lines being pairs, interesting curves are obtained for the second and third pairs. The relative values of the constants in the Maxwell-Sellmeier formula are obtained, and similar conclusions drawn from them as in the case of the paper already referred to concerning the numbers of atoms taking part in the absorption of light. Measurements of wave-lengths of the lines of the principal series are given, and these are shown to be in good agreement with the values calculated from the Hicks modification of the Rydberg formula. Similar measurements were made in the case of sodium. In this case the effects are not so large or so easily obtainable as in the cases of rubidium and potassium. Measurements were also made to see if any temperature effect could be detected in the ratios of the constants of the dispersion formula. These go to show that the ratios m_1/m_2, m_2/m_3, &c., where m_1 m_2, &c., are the constants corresponding to the first, second, &c., lines of the principal series, increase with increase of temperature. This result is what might be expected if the absorbing atoms are ordinary atoms to which corpuscles become attached, more complex systems corresponding to higher members of the series of lines in the spectrum.

"*Ionic Solubility Product.*" By J. Kendall, B.Sc.

Previous investigations upon the simultaneous solubility in water of two substances containing a common ion have been confined to those cases in which the substances examined have been of the same type—*i.e.*, either both strong or both weak electrolytes. In each case the experimental results have been considered to be consistent with the hypothesis of a constant ionic solubility product, although, even in dilute solutions, the agreement is only approximate.

The primary object of this research was to test the applicability of the theory to substances of opposite types, one strong and one weak electrolyte. Preliminary experiments showed that here also small divergences were obtained. Finally, a series of experiments on all the possible types of combination of two electrolytes was carried out, first with dilute and afterwards with more concentrated solutions, in order to ascertain the cause of these divergences and their bearing upon the solidity of the theory,

The results obtained show that the mutual solvent actions of the two substances play an important part in the equilibrium. The general rule appears to be that two substances chemically similar in character give results in excess of theoretical, while with two chemically dissimilar a diminution is observed. In dilute solutions all divergences are small, but fundamental, and in certain cases the amount due to each of the two substances is calculated. In the more concentrated solutions, where the solvent effect is greater, the three possible types of solubility curves are obtained and discussed, and it is found that in all cases experimental divergences from values indicated by the constant solubility product hypothesis can be fully accounted for by this solvent effect of the substances upon each other.

"*Note on the Electrical Waves occurring in Nature.*" By W. H. Eccles, D.Sc., and H. Morris-Airey, M.Sc.

The occurrence of a lightning stroke must, in general, give rise to either a solitary electric wave or a train of electric waves which will be propagated from the centre of discharge to unknown distances. These vagrant waves join with other natural electric phenomena to cause disturbances—technically called "atmospherics"—in the receiving circuits of wireless telegraph stations. Among these other phenomena may be mentioned charged hail or rain striking the air-wires, and earth-air currents. The present communication describes an endeavour to determine the proportion of atmospherics of distant origin.

The plan of attack was as follows:—One of the authors in London and the other in Newcastle arranged receiving apparatus just as for the telephonic reception of signals, and simultaneously listened, at pre-arranged times, for atmospherics. A hand record of the time and intensity of each strong atmospheric was made on paper ruled to represent ten seconds of time per inch. By arranging the periods of observation to include the midnight time signals from the Eiffel Tower or from Norddeich, the time records of the two observers could be accurately co-ordinated. The observers exchanged copies of their records, and counted the number of marks coinciding in time. The results tend to show that about 70 per cent of the atmospherics audible at two stations 270 miles apart, are due to vagrant waves propagated from electrical discharges that take place at (possibly) very great distances.

"*Action of Animal Extracts on Milk Secretion.*" By Prof. A. E. Schäfer, F.R.S., and K. Mackenzie.

Ordinary Meeting, March 16th, 1910.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Gametogenesis of the Gall-fly* (Neuroterus lenticularis)." (Part II.). By L. Doncaster, M.A., Fellow of King's College, Cambridge.

"*Action of the Venom of* Echis carinatus." By Sir Thomas R. Fraser, M.D., F.R.S., and Jas. A. Gunn, M.A., M.D.

"*Further Researches on the Development of* Trypanosoma gambiense *in* Glossina palpalis." By Colonel Sir David Bruce, C.B., F.R.S., A.M.S.; Capts. A. E. Hamerton, D.S.O., and H. R. Bateman, R.A.M.C.; and Capt. F. P. Mackie, I.M.S. (Sleeping Sickness Commission of the Royal Society, Uganda, 1908-10).

"*Spontaneous Cancer in Mice.*" By M. Haaland, M.D., Imperial Cancer Research Fund.

FARADAY SOCIETY.

Ordinary Meeting, March 14th, 1911.

Dr. J. A. Harker, F.R.S., in the Chair.

A paper on "*Some Properties of Aluminium Anode Films,*" by G. E. Bairsto, M.Sc., B.Eng., and R. Mercer, B.Eng., was read in abstract by the Secretary.

This paper gives a preliminary account of an extended investigation that is being made into some of the properties of aluminium anode-films, with special reference to the capacity of such films, and to their behaviour in several electrolytes that have not, previous to this, been used to "form" them.

1. The differences found in the results of previous observers for the capacity of Al anodes are explained by the experimental difficulties involved in messuring the capacity of a very leaky condenser, and by the influence of the length of the period of formation.

Using Sumpner and Record's very accurate method of adapting a Sumpner wattmeter to the measurement of capacity, it was found that the capacity decreases slowly with the time of formation for several days. The higher the formation voltage, the longer is the time required for the capacity to fall to its minimum value. The product of the capacity per sq. cm. and the formation voltage is not constant, but decreases with E, ranging from 8·1 to 6·9

for the range of voltage 10 - 119·5. The electrolyte used was conc. $Am_2B_4O_7$.

2. From the analysis of the measurements made by various observers of the dimensions of the films, and from the thicknesses calculated from the capacity, it is concluded that the film is composed of an inner thin dielectric stratum, which is independent of the electrolyte, enclosed by an outer and much thicker conducting film, varying with the electrolyte. The inner film is supposed to be oxygen in the liquid state.

3. A study of the valve action of the following electrolytes of bivalent or higher acid radicals, K_3FeCy_6, K_4FeCy_6, AmH_2AsO_3, Am_2HAsO_4, and $(Am_2O)_3 7MoO_3$, shows that with the exception of the last none are of any use for building up a high insulation resistance. With AmH_2AsO_4 it was found impossible to rise above 14 volts without extensive pitting taking place; the addition of AmOH to the extent of about 5 per cent completely stopped the pitting, and it was then possible to reach a voltage of 400. There are three points of interest on the volt-resistance curves:—

(1) A point at which maximum resistance occurs;
(2) The critical voltage, at which no reduction from the first value of the current on closing the circuit takes place, but instead an increase;
(3) The breakdown voltage.

4. It is shown that the law of increase of leakage current with temperature is an exponential one, $i = Ae^{at}$, where "a" varies with the period of formation but is independent of the electrolyte; $(Am_2O)_3 7(MoO_3)$ is very much less susceptible to increase of temperature than Am_2BO_7.

5. The effect of the presence of salts which exhibit little or no valve action on the leakage current of Al anodes in $NaAmHPO_4$ showed that in a particular case the addition of the impurity anion in the cases of KCl and KBr to the extent of one-fifth of the PO_4 ion increased the leakage current more than thousandfold. $NaHCO_3$ (a divalent salt) had nothing like this effect.

6. Experiments were made with alternating currents employing a constant e.m.f. and a variable series resistance, with increasing volts across valve cell; it was found that the current was constant over a considerable range of voltage, the volt-current curves for a number of electrolytes being parallel to the axis of voltage. This is explained by the fact that the capacity decreases as the voltage rises; at the same time the resistance increases. The result is that the effective admittance is practically inversely proportional to the voltage.

7. The effect of temperature on the capacity of anodes in $Am_2B_4O_7$ and Na_2HPO_4 was investigated, and it is shown that, contrary to the opinion of McGordan, temperature has considerable influence. Each electrolyte behaves in a characteristic manner, and Na_2HPO_4 gives on the whole a decrease of capacity with temperature, while $Am_2B_4O_7$ gives a considerable increase, a large proportion of which persists on cooling down to normal temperature again.

Prof. W. W. Haldane Gee (communicated) drew attention to the technical importance of the subject in connection with electrolytic condensers, rectifiers, and lightning protectors. He referred to anode films which he had produced on platinum, and which he believed were films of oxygen. The ordinary aluminium films are electro-negative to zinc in water, but on heating the films disappear and the aluminium becomes electropositive; on cooling again the film reforms and a hysteresis loop is obtained on plotting the observations. The occurrence of the critical point in many of the authors' curves between 35° and 40° C. was noteworthy (see *Trans. Farad. Soc.*, July, 1910, vi., [1], p. 64).

Dr. W. C. McC. Lewis criticised the assumption that the specific inductive capacity of the dielectric portion of the film was unity. This probably led to the discrepancy between the measurements of the film-thicknesses obtained by the direct and indirect methods.

A paper on "*The Weight of a Normal Litre of Hydrogen Chloride*," by F. P. Burt, B.Sc., and R. W. Whytlaw-Gray, Ph.D., was read by Mr. Burt. (Will be inserted in full).

Mr. Ernest Vanstone, B.Sc., read a paper entitled "*A Physical-chemical Study of Mercury-sodium Alloys or Sodium Amalgams.*" (Will be inserted in full).

Mr. S. W. J. Smith, M.A., D.Sc., and Mr. W. F. Higgins, B.Sc., read a paper "*On Surface Effects between Mercury and certain Solutions and an Electrochemical Method of Estimating Dissolved Oxygen.*"

The effects of small quantities of Na_2S upon the potential difference between mercury and dilute solutions of various electrolytes have been studied and an attempt has been made to analyse and explain them.

The rate of change of potential difference resulting from addition of Na_2S is at first roughly proportional to the amount of Na_2S added, but suddenly increases at a critical concentration lying near 0·0004 equivalents Na_2S per litre in solutions containing about 0·0011 equivalents of O per litre.

This effect is temporary and almost disappears within twenty-four hours. It is replaced by a similar effect, permanent so long as atmospheric oxygen is excluded, which occurs in the solution containing initially about 0·00055 equivalents Na_2S per litre.

The second effect is due to the conversion of the Na_2S into $Na_2S_2O_3$, by interaction with the oxygen contained in the solution. The amount per litre of Na_2S required to produce the effect is thus a measure of the amount per litre of the dissolved oxygen. A very slight excess is sufficient to alter the potential difference by more than half a volt.

The temporary effect is apparently due, partly at least, to selective adsorption of Na_2S at the mercury surface.

The experiments illustrate incidentally the origin of phenomena analogous to the "oxidation tints" of tempered steel.

NOTICES OF BOOKS.

The Encyclopædia Britannica: A Dictionary of Arts, Sciences, Literature, and General Information. Eleventh Edition. Cambridge: At the University Press. 1910.

(Chemistry, Geology, Agriculture).

The sections on Chemistry, Geology, and Agriculture in the eleventh edition of the Encyclopædia Britannica have not merely been thoroughly revised, but the general plan and scope of them have undergone a profound alteration, which adds immeasurably to their usefulness both for the general reader and for the specialist. In the general articles on the three sciences such information is given relating to the history and main principles as to enable them to be readily understood and assimilated by an elementary student, or by a reader who has practically no previous knowledge of the subject. In the article on Chemistry, for instance, the development of the science is traced from its alchemistic beginnings to the foundation of the modern theory; the general principles are discussed in a section in which the fundamental laws of chemistry and the use of formulæ and equations are explained; descriptive inorganic and organic chemistry are treated in the broadest outline, and analytical and physical chemistry are briefly reviewed.

The article under the heading of Geology is similarly divided into parts in which are discussed the history of the science, its cosmical aspects, geognosy, &c. The whole of it is written in the very lucid and interesting style which is familiar to readers of the books and papers which have come from the pen of its contributor (Sir Archibald Geikie), and in it special attention is paid to such matters as physiographical geology which are not treated elsewhere;

the summary of historical geology, dealing with the development of geological conceptions from the time of the Greeks and the Romans to the present day, will be greatly appreciated.

In the leading article on Agriculture its history is traced, and the chief aspects and tendencies of the industry are discussed with special reference to the United States and the United Kingdom, but technical processes and methods of cultivation are not dealt with.

In all three subjects the leading articles give as complete an account as can reasonably be expected, and provide epitomes of knowledge such as are not to be found in the text-books; they are skilfully put together, and interest has not been sacrificed to extreme conciseness, while no essential points have been overlooked. The information in them is not only the most recent that could be obtained, but it is also presented from a modern point of view.

To supplement these general articles the eleventh edition contains a great number of short articles to which the reader may refer for information upon a special branch or subject, if he does not want to read through the whole general article, or if he requires fuller details than are deemed suitable for inclusion in the general article. These shorter articles include a great number of biographies in which sympathetic and appreciative accounts are given of the life and work of some of the foremost scientific men, both of the present day and of the past. In chemistry each of the elements is discussed in one such special article, in which full accounts are given of the preparation, properties, and uses of the element and its most important compounds, the determination of its atomic weight, and its uses in medicine, which are treated particularly fully. The other articles comprise many on important organic and inorganic compounds, and on some general subjects such as dissociation, combustion, flame, &c.; these articles are mostly excellently arranged summaries from which the reader can get a clear idea of the exact state of our knowledge at the present moment, and can at the same time gather some information as to the problems still awaiting solution. The article on Alloys is a good example of these shorter articles in which the essentials are exceedingly clearly stated and well illustrated. The modern theory of the ether is also well treated in a very stimulating and interesting article.

In Agriculture the chief technical processes are separately treated in considerable detail, and the cultivation of each important crop is described; sections are added upon the farm animals, with information as to breeds, management, &c. The Soil is treated by Professor John Percival, and Manures and Manuring by Professor J. A. Voelcker, in sections which are thoroughly practical and eminently readable.

In general, it may be said that the portions of the Encyclopædia dealing with the three sciences satisfy all reasonable requirements; the new arrangement has added very greatly to their usefulness, and the excellent system of cross references which has been adopted considerably increases the facility with which information can be found. At the same time overlapping has been successfully avoided, and the utmost use has been made of every inch of space.

Royal Institution.—On Thursday next, April 6th, at 3 o'clock, Prof. W. A. Bone, F.R.S., will deliver the second of his course of two lectures at the Royal Institution on "Incandescent Surface Combustion and its Industrial Applications."

Measurement of Surface Tension.—R. Magini.—Even pure air produces a decrease of the surface tension of water amounting to at least 1 per cent. Equimolecular solutions of the two stereoisomers investigated (fumaric and maleic acids) have the same surface tension. The surface tension of absolute alcohol is a linear function of the temperature until the melting-point is reached.—*Atti della Reale Accademia dei Lincei*, xx., No. 1.

OBITUARY.

PROFESSOR JOHN ATTFIELD, F.R.S.

The late Professor Attfield, whose death was announced in the last number of the Chemical News, was born in 1835, and educated at Barnet. He early showed his aptitude for the study of chemistry, and on leaving the Pharmaceutical Society with high honours in 1854 he became Demonstrator of Chemistry at St. Bartholomew's Hospital, where he remained until 1862, when he was appointed Professor of Chemistry to the Pharmaceutical Society. This post he held until 1896. He was an active member of the British Pharmaceutical Conference, and a member of the Council of the Chemical Society from 1874 to 1878, as well as a member of the Council of the Institute of Chemistry; he was instrumental in bringing about the imperialisation of the British Pharmacopœia and acted as its editor for many years.

While still Demonstrator of chemistry at St. Bartholomew's Hospital he made some important contributions to chemical knowledge. Thus, in 1860 he read his first paper before the Pharmaceutical Society on the "Adulteration of Carmine," in which he described the results of analyses of samples which had been largely adulterated with vermilion and lead dichromate, and discussed tests of the purity of the substance. In the same year he contributed to the Chemical News a paper describing the results of the thorough investigation of the solubility of mercury precipitates in solutions of salts of ammonium. Thenceforward he continued to make frequent reports on the research work which he undertook with much zest and with conspicuous success. Thus he studied the spontaneous oxidation of oils, dealing specially with cod-liver oil, and in 1862 read an important paper before the Pharmaceutical Society on the mineral constituents of plants. In this paper he urged the value of microscopic analysis and the use of the process of dialysis to obtain crystals of the salts contained in the ashes of plants. Two years later he described the continuation of his dialytic experiments before the Pharmaceutical Conference, and gave the results of the application of the process to the juices of many common crops. In 1863 he read before the Chemical Society a paper on the preparation of oxamide from hydrogen peroxide and hydrocyanic acid, which reaction he thoroughly elucidated, and in the same year described to the Pharmaceutical Society his very important method of dissolving alkaloids, *e.g.*, quinine, in oils by first preparing the oleate of the alkaloid.

Professor Attfield took an active part in the discussions at the meetings of the Pharmaceutical Society, and did a great deal to increase the value and the usefulness of the British Pharmacopœia. In 1864 he delivered two lectures on the relation of the British Pharmacopœia to pharmacology, in which he criticised the decisions of the compilers in a very outspoken way, drawing special attention to their failure to cope successfully with the difficulty of giving the latest information with regard to preparations and compounds. In later papers he discussed the assay of coal for crude paraffin-oil and petroleum, and the determination of the ignition-point of petroleum, and in 1871 he made important suggestions with regard to the improvement of the nomenclature of pharmacology, necessitated by the advance of chemical knowledge. He also published many notes on the results of his analyses of various articles of food and waters from different sources; thus he investigated Dika bread, Kola nut, &c., and analysed the water of a Jamaican spring which had remarkable medicinal properties.

Besides these numerous papers, and in spite of his arduous labours as the editor of the British Pharmacopœia and of the Indian and Colonial Addendum to the Pharmacopœia, he was the author of two important text-books, of which the best known was "Chemistry, General, Medical, and Pharmaceutical." The first edition of this

book was published in 1867, and it was so greatly appreciated that fresh editions were repeatedly issued; it held its own against all competitors for many years, reaching its eighteenth edition in 1903 and its nineteenth in 1906. He wrote also a treatise on Water and Water Supplies.

The value of Professor Attfield's work on pharmacology was fully recognised by all the most important Pharmaceutical Societies in Europe and America, many of which elected him an honorary member, and he was a Fellow of the Royal Society and a Ph.D. of the University of Tübingen. Of late years he had retired from active work, but his services to pharmacology probably excelled those of any other chemist. He brought great scientific talent and power of organisation to bear upon the study of drugs and medicines, and for his work with regard to the British Pharmacopœia alone deserves to rank among the foremost men of science whose death will be deplored in foreign countries as well as in England.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliı., No. 5, January 30, 1911.

Density, Coefficient of Dilatation, and Alteration of Volume on Fusion of the Alkali Metals.—Louis Hackspill.—The following table gives the results of the author's determinations of the physical constants of the alkali metals:—

Cæsium.

Density at 0°	1·9029
Coefficient of dilatation in solid state	0·000291
Coefficient of dilatation in liquid state (28—50°)	0·000341
Coefficient of dilatation in liquid state (50—123°)	0·000348
Percentage increase of volume on fusion	2·32

Rubidium.

Density at 0°	1·5248
Coefficient of dilatation in solid state	0·00027
Coefficient of dilatation in liquid state (40—140°)	0·000339
Percentage increase of volume on fusion	2·28

Potassium.

Density at 0°	0·859
Coefficient of dilatation in solid state (0—58°)	0·00025
Coefficient of dilatation in liquid state (70—100°)	0·000280
Coefficient of dilatation in liquid state (100—150°)	0·000285
Percentage increase of volume on fusion	2·42

Sodium.

Density at 0°	0·9725
Density at 96·5°	0·9385
Coefficient of dilatation in solid state (0—80°)	0·000216
Coefficient of dilatation in liquid state (100—180°)	0·000275
Percentage increase of volume on fusion	1·50

Photolysis of Complex Acids by Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—Whatever the physical state of a substance (gaseous, solid, liquid, or dissolved) its decomposition by ultra-violet rays takes place in the same way. The complex linear acids in which the acid function is joined to an oxygenated function exhibit a tendency to be decomposed by light with formation of carbon dioxide. The salts of uranium increase the volume of gas disengaged in photolysis without altering the products, and the catalytic action appears to be a phenomenon of photochemical resonance.

Green Crystallised Manganitartrate.—A. Job and P. Goissedet.—When air acts on manganous hydrate dissolved in sodium tartrate a manganic compound is formed, oxygen being fixed by the excess of tartrate. The solution which is thus obtained is red, but it gradually loses its colour and green crystals are precipitated from it. The composition of these crystals appears to be represented by the formula—

$$\begin{array}{l} \mathrm{COONa{-}CHO{-}CHO{-}COONa} \\ \qquad\qquad\quad \diagdown\ \ \diagup \\ \qquad\qquad\quad \mathrm{Mn} \qquad +11\mathrm{H_2O} \\ \qquad\qquad\quad \diagup\ \ \diagdown \\ \mathrm{COONa{-}CHO{-}CHONa{-}COONa.} \end{array}$$

Apparently the green compound is dissociated in water into two simple molecules, one consisting of alkaline tartrate and the other of red manganic tartrate; excess of the alkaline tartrate retards this dissociation and makes the green complex stable.

Action of Chlorides of α-Alkoxyl Acids on Mixed Organometallic Compounds of Zinc.—E. E. Blaise and L. Picard.—When the chlorides of α-alkoxyl acids act on the mixed organo-metallic compounds of zinc some ether oxide is first formed, and then reacts normally according to the equations:—

$$\mathrm{R\ O{-}CH_2{-}CO{-}Cl + R{-}O{-}CH_2Cl + CO,}$$
$$\mathrm{R{-}O{-}CH_2Cl + R'{-}Zn\ I = ZnICl + R{-}O{-}CH_2{-}R'.}$$

The higher the temperature the greater the quantity of ether oxide formed, and the yield of oxide also tends to increase as the weight of the alkyl of the organo-zinc compound increases. If the radical of the organo-zinc compound is cyclic only the ketonic derivative can be isolated. The variation of the alcoholic radical of the ether oxide function of the acid chloride modifies these results considerably.

α-Bromcrotonic Aldehyde.—P. L. Viguier.—α-Bromcrotonic aldehyde readily yields an oxime and a semicarbazone. With hydrazine it gives 5-methylpyrazol, and with phenyl hydrazine a phenyl hydrazone. It reacts with urethane to give a compound of formula $C_{13}H_{24}O_6BrN_3$.

New Derivatives of Indene.—V. Grignard and Ch. Courtot.—With C_2H_5MgBr indene gives an organo-magnesium derivative, from which by oxidation α-indenol is obtained. α-Indene carboxyllic acid can also be prepared from it, and it gives condensation products with fluorenone and benzophenone.

MEETINGS FOR THE WEEK.

MONDAY, 3rd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Measurement of High Temperatures," by C. T. Heycock. "Gum from the *Bombax Malabaricum*," by P. P. Phillips.
TUESDAY 4th.—Royal Institution, 3. "Explorations of Ancient Desert Sites in Central Asia," by M. Aurel Stein.
—— Royal Society of Arts, 4.30. "The Commonwealth of Australia," by Capt. R. M. Collins, R.N., C.M.G.
WEDNESDAY, 5th.—Society of Public Analysts, 8. "Analytical and Microscopical Examination of Compound Liquorice Powder," by G. E. Scott-Smith and J. Evans. "Almond and Apricot Kernel Oils" and "Constants of Chicken and Turkey Fats," by R. Ross and J. Race. "Gerber's 'Neusal' Milk Test" and "Abnormal Cotton Cakes," by J. Goulding. "Further Contribution to the Question of Turpentine Substitutes," by J. H. Coste and L. M. Nash.
—— Royal Society of Arts, 8. "Wheels, Ancient and Modern, and their Manufacture," by H. L. Heathcote, B.Sc.
THURSDAY, 6th.—Royal Institution, 3. "Surface Combustion and its Industrial Applications," by Prof. W. A. Bone, F.R.S.
—— Royal Society, 4.30. (Bakerian Lecture). "Chemically Active Modification of Nitrogen produced by the Electric Discharge" (illustrated by Experiments), by Prof. the Hon. R. J. Strutt, F.R.S.
—— Chemical, 8.30. "Constituents of Rhubarb," by F. Tutin and F. W. B. Clewer. 6-Nitro-3:4:3':4'-tetramethyldiphenyl," by A. W. Crossley and C. H. Hampshire. "Diphenylene, a New Aromatic Hydrocarbon," by J. J. Dobbie, J. J. Fox, and A. J. H. Gange. "Correlation of Viscosity with other Physical Properties—Part I., Ethenoid and Ethinoid Unsaturation," by T. P. Hilditch and A. E. Dunstan. "Chemical Action induced by Cathode Rays and Canal Rays," by E. P. Perman.
FRIDAY 7th.—Royal Institution, 9. "A New Method of Chemical Analysis," by Prof. Sir J. J. Thomson, F.R.S.
SATURDAY, 8th.—Royal Institution, 3. "Radiant Energy and Matter," by Prof. Sir J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. CIII., No. 2680.

SULPHITE METHOD FOR SEPARATING AND IDENTIFYING STRONTIUM AND CALCIUM.

By J. I. D. HINDS.

The difficulty which beginners in qualitative analysis experience in the separation and identification of strontium and calcium have led me to seek a method which might be easier and more satisfactory than those now in use. By a study of the table of aqueous solubilities we learn that strontium sulphite is sparingly soluble (0·033 grm. to the litre), while calcium sulphite is quite soluble (1·2 grm. to the litre), and that strontium sulphite is considerably less soluble than strontium sulphate (0·11 grm. to the litre). As to barium and strontium sulphites, the difference in solubility is small and not sufficient for separation. All these solubilities are increased in acid solutions, but not to the same degree. In the presence of sufficient hydrochloric acid barium ion is precipitated by sulphite ion, while strontium ion is not; in dilute acetic acid solution barium and strontium ions are precipitated, while calcium ion is not.

In this investigation I used a freshly prepared concentrated (nearly saturated) solution of sodium sulphite. If the solution is kept long the sulphate in it is increased by oxidation and the reactions are not typical. In finding the precipitation limits I used standard solutions of strontium and calcium chlorides.

In order to compare the efficiency of the commonly used calcium sulphate with that of sodium sulphite, which I propose as the precipitant, I diluted the strontium solution to various degrees of concentration with water containing a slight excess of acetic acid and a sufficient quantity of the reagent, in the one case calcium sulphate and in the other sodium sulphite, bringing the mixture to boiling and letting it stand for a few minutes. The following results were obtained:—

Concentration of strontium solution.	Reagent. $CaSO_4$.	Na_2SO_3.
0·00005 normal	No precipitate	Faint cloud
0·0001 ,,	,,	Slight precipitate
0·0005 ,,	,,	Precipitate
0·001 ,,	,,	,,
0·004 ,,	Faint cloud	,,
0·005 ,,	Precipitate	,,

It is thus seen that the sulphite ion in the presence of a slight excess of acetic acid will give a precipitate in a ten-thousandth normal solution of strontium ion (0·004 grm. to the litre), while calcium sulphate requires a concentration 0·005 normal (0·2 grm. to the litre); that is, the sulphite is about fifty times as sensitive as the sulphate in grms. of strontium ion to the litre. In solutions more strongly acid the difference is greater, though the sensitiveness is diminished.

The strontium and calcium solutions yielded with ammonium oxalate the following results:—

Concentration.	Calcium.	Strontium.
0·0005 normal	No precipitate	No precipitate
0·0007 ,,	Faint cloud	Faint cloud
0·001 ,,	Precipitate	Precipitate

The sensitiveness of the calcium and strontium ions to the oxalate ion thus appears to be about the same, and the precipitation limit is not far from that of strontium sulphite. This relationship is but little changed in the presence of acetic acid, though the sensitiveness is diminished.

The precipitation limits for the sulphites of calcium and strontium were then determined under four conditions:—(1) With the sulphite solution alkaline by hydrolysis, cold; (2) the same boiled; (3) the sulphite solution made slightly acid with acetic acid and the mixture boiled; (4) the sulphite solution made more strongly acid, and the mixture boiled.

1. The sulphite solution alkaline, cold, without acid, the mixture well shaken:—

Concentration.	Calcium.	Strontium.
0·0005 normal	No precipitate	No precipitate
0·001 ,,	,,	Faint cloud
0·0015 ,,	,,	Precipitate
0·002 ,,	,,	,,
0·006 ,,	,,	,,
0·008 ,,	Faint cloud	,,
0·01 ,,	Precipitate	,,

2. Sulphite solution alkaline and the mixture boiled:—

Concentration.	Calcium.	Strontium.
0·00005 normal	No precipitate	Faint cloud
0·0001 ,,	,,	Precipitate
0·0005 ,,	Faint cloud	,,
0·001 ,,	Precipitate	,,

We thus see that the alkaline sulphite makes a rather complete precipitation of both the calcium and the strontium.

3. The sulphite solution slightly acid with acetic acid, the mixture boiled:—

Concentration.	Calcium.	Strontium.
0·0005 normal	No precipitate	Faint cloud
0·001 ,,	,,	Precipitate
0·003 ,,	,,	,,
0·005 ,,	Precipitate	,,

4. The sulphite solution strongly acid with acetic acid, the mixture boiled:—

Concentration.	Calcium.	Strontium.
0·0005 normal	No precipitate	No precipitate
0·001 ,,	,,	,,
0·0015 ,,	,,	Precipitate
0·01 ,,	,,	,,
0·1 ,,	,,	,,
1·0 ,,	,,	,,
1·2 ,,	Cloud	,,
1·3 ,,	Precipitate	,,

With acid of this strength the concentration of the filtrate is only 0·001 normal in strontium, while it is 1·3 normal in calcium. If the solution is not higher than this in calcium the separation of the calcium and strontium is almost complete. If the solution is stronger, more acid may be added and still the separation will be good, since the strontium is practically all precipitated when the mixture is boiled, even in the presence of much acid. When the salts are mixed some calcium remains in the precipitate, possibly because of oxidation to sulphate, which seems to be less soluble in the acid than the sulphite.

The quantity of strontium which remains in the solution after the precipitation with the sulphite in the presence of acetic acid is just at the precipitation limit of strontium oxalate, and the filtrate will give no precipitate with ammonium oxalate, or only a faint cloud. If it be diluted with an equal quantity of water no precipitate falls. On the other hand, the calcium has largely remained in solution and will be precipitated by the oxalate ion. Calcium is thus sharply and easily separated from strontium. The strontium precipitate may contain some calcium from which it is not easily separated. It will generally be satisfactorily identified by the flame reaction as described below.

Guided by the above facts, I have devised a modified method of analysis for the barium group which in repeated trials by myself and my students has been found to be eminently practical and easy.

1. Precipitate the elements of the group as carbonates, wash and dissolve in the least quantity of warm dilute acetic acid in the usual way.

2. *Preliminary Testing.*—(*a*) Add to 1 cc. of the solution in a test-tube a few drops of hydrochloric acid, then 1 cc. of a freshly prepared concentrated solution of sodium sulphite. A precipitate is barium sulphite, proving the presence of barium. (*b*) Add to 1 cc. of the solution a few drops of dilute acetic acid, then 1 cc. of the sulphite solution. A precipitate is barium or strontium sulphite ; in the absence of barium, can only be strontium. (*c*) If barium and strontium are absent, add to 1 cc. of the solution 1 cc. of the sulphite. A precipitate is calcium sulphite, easily soluble in acetic acid.

3. Remove barium ion, if present, with dichromate ion, and free the filtrate from dichromate ion by precipitation as carbonate and solution in dilute acetic acid in the usual way. The removal of the dichromate ion is generally not necessary as the reactions are not seriously disguised by it.

4. To 5 cc. of the solution of 3 (or of 1 if barium is absent) add about 3 cc. of the sulphite solution, or enough or complete precipitation. A precipitate may be calcium or strontium sulphite. No precipitate does not indicate their absence. In either case add about 1 cc. of dilute acetic acid, or just enough to dissolve or nearly dissolve the precipitate. Avoid much excess. If much strontium s present it will not dissolve. Heat to boiling, and set aside until the precipitate has mostly subsided. Pour the quid on a filter, leaving the bulk of the precipitate in the test-tube. If the filtrate is cloudy, pass it through the filter again and again until it is perfectly clear.

The filtrate will contain most of the calcium and very little strontium.

The precipitate is strontium sulphite, but may contain some calcium sulphite.

5. Add to 5 cc. of the filtrate of 4 a little ammonium oxalate solution. A precipitate is calcium oxalate. If there is only a faint cloud it may be due to strontium. In this case, dilute another portion of the filtrate with an equal quantity of water, and add the oxalate. The precipitate must be calcium oxalate, since the strontium concentration has been reduced below the precipitation limit of strontium oxalate.

6. Cover the precipitate of 4 in the test-tube with hydrochloric acid, and heat to boiling. Test on platinum wire in the flame for strontium. If much calcium is present there may be enough in the precipitate to mask the strontium flame. In this case a very sharp distinction can be made as follows :—Use two platinum wires, dipping one in a pure hydrochloric acid solution of a calcium salt and the other in the solution to be tested. Insert the middle of the wires in opposite sides of the Bunsen flame near its base, and draw them slowly forward until the looped ends are in the flame. The sodium (and potassium if dichromate has been used) burns off first and leaves the more persistent calcium and strontium in the flame. A decided difference in the flame colours thus brought side by side is caused by even a trace of strontium.

7. For further confirmation of strontium add calcium sulphate solution to a portion of the solution of 3, and boil. A slowly forming precipitate indicates strontium.

The chief advantage of this method lies in the easy and unmistakable identification of calcium in the presence of strontium.

University of Nashville,
Nashville, Tennessee.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 11th and 12th, 1911, commencing each day 10.30 o'clock a.m.

THE CHEMICAL SIGNIFICANCE OF CRYSTAL STRUCTURE.*

By Prof. WILLIAM J. POPE, M.A., F.R.S

(Concluded from p. 152).

Having shown that the crystalline forms of the elements are in complete harmony with the conception that crystal structures can be homogeneously divided into similar cells of polyhedral shapes approximating closely to the spherical, reference may now be made to some simple compounds, those, namely, in which the molecule consists of two dissimilar atoms.

The conception of the equilibrium of centred forces which has been shown fertile in the case of the crystalline elements can be immediately applied to the binary compounds ; as before, each atom will be represented by forces emanating from a centre, and equilibrium will demand closest packing of the spheres used, just as in the previous case. The atomic centres will now, however, be of two kinds, and the question arises as to whether the domains of atomic influence to be described about them will be all of the same magnitude or whether two magnitudes of spheres must be employed, one for each element present. This question is difficult to answer by reference to the facts already reviewed above ; probably the only indication which the latter afford in this connection is that closest-packing of a considerable variety of different magnitudes would certainly be most unlikely to lead to the close similarity of crystal form observed as between the elements and the binary compounds. A direct answer is, however, provided as the result of investigating the crystalline forms of organic substances, to which reference will presently be made ; this investigation has led to the discovery of a definite law which governs the magnitudes of the several kinds of atomic domain concerned in any crystalline compound substance. It is found that the magnitudes of the atomic domains in any crystalline compound are very approximately in the ratio indicated by the fundamental valencies of the corresponding elements. Since the molecules of nearly all the binary compounds which have been crystallographically examined contained in the molecule one atom each of two elements of the same valency, the polyhedral cells from which a crystalline binary compound must be supposed built up are all, in general, of approximately the same magnitude. The fact that most binary compounds, like most elements, crystallise in either the cubic or the hexagonal system, represents one of the simple results of this law of valency volumes.

The binary compounds thus, in general, affect crystalline structures which are derived from the cubic or the hexagonal closest-packed assemblage of equal spheres ; one-half of the spheres, selected homogeneously, represent atoms of the one element and the remainder atoms of the second element. The mode in which the necessary homogeneous selection may be made in the cubic assemblage, without altering the values of corresponding dimensions in three rectangular directions, is shown in a model.

The crystalline forms of the binary compounds are in accordance with what has been above foreshadowed. Table I. indicates that in geometrical respects the crystalline binary compounds closely resemble the elements ; 68·5 per cent of those examined are cubic and 19·5 per cent hexagonal, the remaining 12 per cent crystallising in systems of lower symmetry than these. The axial ratios, $a : c$, of all the hexagonal binary compounds known are stated in Table II. ; all approximate closely to the value, $a : c = 1 : 0{\cdot}8165$, for the model hexagonal closest-packed assemblage of equal spheres.

In connection with the elements and binary compounds it is noteworthy that the mode of treatment described

* A Discourse delivered at the Royal Institution, April 15th, 1910.

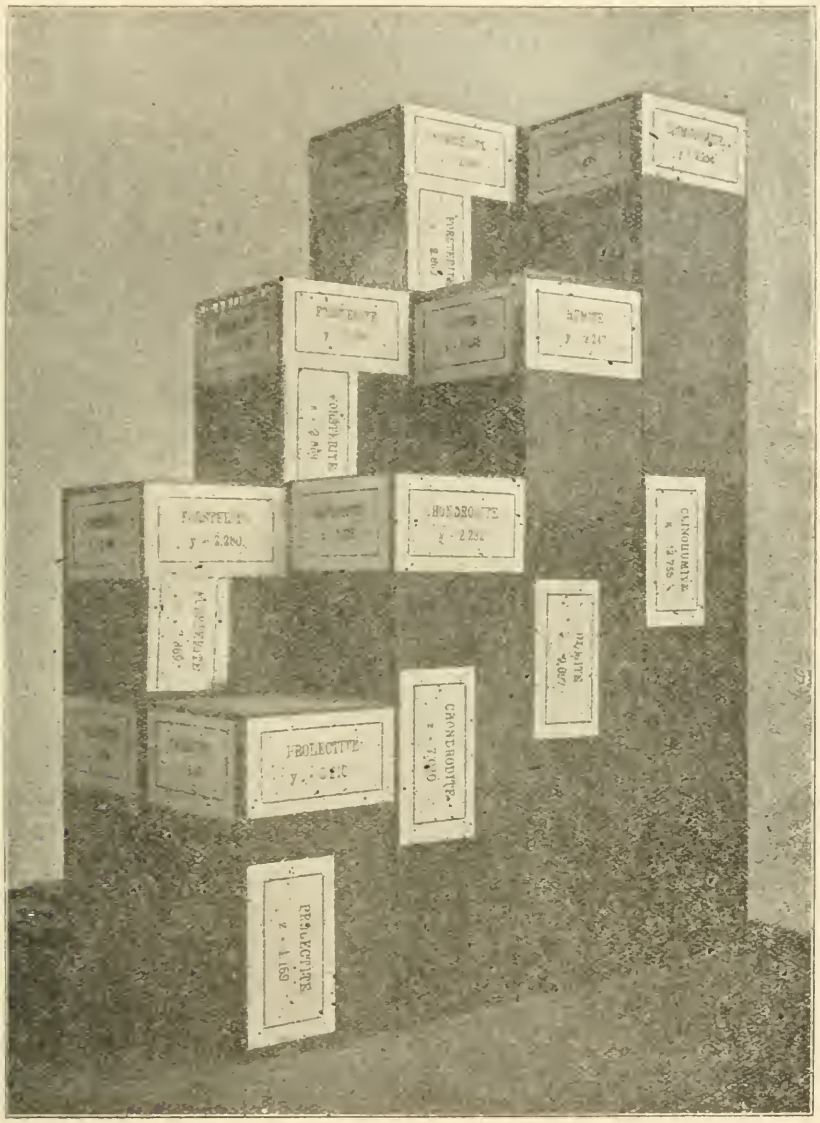


Fig. 5.

appears practically to eliminate molecular aggregation of the atoms as a factor in determining the crystalline structure; that is to say, the distance separating two neighbouring atom centres is the same whether those atoms belong to the same or to different molecules. Another interesting fact is that, whilst the elements and binary compounds for the most part crystallise in the cubic or hexagonal systems, substances of greater molecular complexity rarely crystallise in these highly symmetrical systems; thus, of a great number of organic compounds examined, 2·5 and 4·0 per cent only belong to the cubic and hexagonal crystalline systems respectively (Table I.). This observation is important as one of many indications that the cells into which the crystal structure of a complex compound are partitionable are not, in general, all of the same volume. Further investigation shows that the volumes of the polyhedral cells representing the atomic domains of the several elements present in a complex crystalline compound are governed by the law of valency volumes to which reference has already been made. The correctness of this conclusion concerning the proportionality between the numbers expressing the fundamental valencies of the elements and the volumes of the corresponding spheres of atomic influence has been abundantly verified, not only by the laborious process of working out a large number of cases, but in several other ways which may be more rapidly indicated. The following are illustrations of the latter kind of verification.

Table III. states the composition and axial ratios, $a : b : c$, of a series of four crystalline minerals which differ in composition by the increment, Mg_2SiO_4; the sums of the valencies of the atoms composing the different molecular aggregates are stated under the heading W. The increment, Mg_2SiO_4, also occurs as the crystalline

TABLE II.—*Hexagonal Binary Compounds.*

		$a : c$
Beryllium oxide	BeO	1 : 0·8153
Zinc oxide	ZnO	1 : 0·8039
Zinc sulphide	ZnS	1 : 0·8175
Cadmium sulphide ..	CdS	1 : 0·8109
Silver iodide	AgI	1 : 0·8196
The ratio, 1 : $\sqrt{(\frac{8}{3})}$ ..		1 : 0·8165

TABLE III.—*The Humite Minerals.*

Prolectite, $MgSiO_4$,2Mg(F,OH) ..	W = 22
Chondrodite, $Mg_2(SiO_4)_2$,2Mg(F,OH)	W = 38
Humite, $Mg_5(SiO_4)_3$,2Mg(F.OH) ..	W = 54
Clinohumite, $Mg_3(SiO_4)_4$,2Mg(F,OH)	W = 70

The increment is Mg_2SiO_4, namely, forsterite, with W = 16.

	Axial Ratios. $a : b : c$	Equivalence Parameters. $x : y : z$
Prolectite . ..	1·0803 : 1 : 1·8862	2·389 : 2·210 : 4·169
		Diff. = 2·851
Chondrodite .	1·0863 : 1 : 3·1447	2·425 : 2·232 : 7·020
		Diff. = 2·877
Humite . ..	1·0802 : 1 : 4·4033	2·428 : 2·247 : 9·897
		Diff. = 2·858
Clinohumite ..	1·0803 : 1 : 5·6588	2·435 : 2·254 : 12·755
Values for the increment, forsterite.		
Observed . ..	1·0757 : 1 : 1·2601	2·449 : 2·277 : 2·869
Calculated ..	1·0823 : 1 : 1·2775	2·429 : 2·245 : 2·867

mineral forsterite, of which the axial ratios have been determined. It is evident that the ratio, a/b, has approximately the same value of 1·08 for all four members of the series, and that practically all differences in relative dimensions are expressed by the ratio, c/b. On dividing the valency volume, W, by the corresponding value for c/b in each case, the quotients 11·7, 12·1, 12·3, 12·4, and 12·7 are obtained respectively for the substances prolectite, chondrodite, humite, clinohumite, and forsterite. The relative dimension, c/b, is thus roughly proportional to the sum of the valencies in this set of minerals. The comparison may, however, be made more accurately by including the changes in both relative dimensions, a/b and c/b, in the calculation in the following manner. The "equivalence parameters" are the rectangular dimensions, x, y, and z, of a rectangular block having the volume W, and are in the ratio of the axial ratios, $a : b : c$. The parameters x and y preserve almost constant values throughout the series, and addition of the increment, Mg_2SiO_4, leads to a practically constant increase of about 2·86 in the dimension z, on passing from one mineral to the next in the series. The mineral forsterite also gives nearly the same x and y values as before, and its z value, 2·87, is equal to the differences between consecutive pairs of z values in the main series; these differences vary between 2·85 and 2·88. The axial ratios and equivalence parameters of forsterite can indeed be calculated with considerable accuracy from the data available for the series of four minerals.

The relations here displayed may be rendered more obvious by a series of models (Fig. 5). Rectangular blocks having as the horizontal dimensions the x and y values, and as vertical dimension the z value, for forsterite, when superposed upon a similar set of blocks having the corresponding dimensions for prolectite, form a stack exhibiting the equivalence parameters of chondrodite; superposing on this a second set of forsterite blocks leads to a stack showing the equvalence parameters of humite, and on again repeating the operation, a stack with the dimensions of clinohumite results. From the numerical data and the models exhibited it must be regarded as definitely proved that, in this series, the volumes appropriated by the constituent atoms are, in any one member, directly proportional to the valency numbers of the corresponding elements.

Another set of observations of a very convincing character although of a totally different kind is laid out in Table IV.

TABLE IV.—*Molecular Volumes of the Normal Paraffins at their Melting-points.*

	W.	Melting-point $t°$	Molecular volumes. Observed at $t°$	Molecular volumes. Calculated as W × S.
$C_{11}H_{24}$	68	−26·5	201·4	201·96
$C_{12}H_{26}$	74	−12·0	219·9	219·78
$C_{13}H_{28}$	80	− 6·2	237·3	237·60
$C_{14}H_{30}$	86	+ 4·5	255·4	255·42
$C_{15}H_{32}$	92	+10·0	273·2	273·24
$C_{16}H_{34}$	98	+18·0	291·2	291·06
$C_{17}H_{36}$	104	+22·5	309·0	308·88
$C_{18}H_{38}$	110	+28·0	326·9	326·70
$C_{19}H_{40}$	116	+32·0	344·7	344·52
$C_{20}H_{42}$	122	+36·7	362·5	362·34
$C_{21}H_{44}$	128	+40·4	380·3	380·16
$C_{22}H_{46}$	134	+44·4	398·3	398·00
$C_{23}H_{48}$	140	+47·7	416·2	415·80
$C_{24}H_{50}$	146	+51·1	434·1	433·62
$C_{27}H_{56}$	164	+59·5	487·4	487·08
$C_{31}H_{64}$	188	+68·1	558·4	558·36
$C_{32}H_{66}$	194	+70·0	576·2	576·18
$C_{35}H_{72}$	212	+74·7	629·5	629·64

(Mean value of S = 2·970).

Experimental determinations of the molecular volumes of a long series of normal paraffins, made on the liquid substances at temperatures at which the materials are in physically similar conditions, are stated in column 4. Since the valency of carbon is four times that of hydrogen it would be anticipated from the crystallographic conclusions previously drawn, that each carbon atom should appropriate four times as large a space for occupation as one hydrogen atom; the quotient of the molecular volume by the valency sum or valency volume, W, should consequently lead to the same value, S, in the case of all the hydrocarbons.

The mean value of S, namely, the atomic volume of hydrogen, is thus calculated as 2·970, and that it is constant within very narrow limits is seen on comparing volume 4 and 5, the latter of which states the product of the valency volume, W, by the value 2·970. The simple relation between the atomic volumes of carbon and hydrogen in the liquid normal paraffins indicated in the above table was recently pointed out by Le Bas, and is abundantly confirmed by numerous series of determinations in addition to that now quoted. It is thus definitely proved that the law of valency volumes, first enunciated on the ground of the crystallographic evidence, holds rigidly in the case of these liquid substances.

Sufficient has been said to demonstrate that a method has now been devised by means of which the vast stores of accurate goniometric measurements collected by crystallographers during the past century can be interpreted and that the requisite interpretation has in many cases already been given. Prof. Liveing, in a discourse delivered in this room nineteen years ago, suggested that crystalline forms are the outcome of the accepted principles of mechanics; the aid of these, and of these alone, has been invoked to show that crystalline structures result from the equillibrium of the attractive and repulsive forces radiating from the atomic centres.

Royal Institution.—A General Monthly Meeting of Members of the Royal Institution was held on the 3rd inst., The Duke of Northumberland, K.G., President, in the Chair. Mr. J. Devonshire, Mr. G. H. Griffin, Mr. W. E. Lawson Johnston, Mrs. Guy Pym, and Mr. A. E. Reed were elected Members. The Chairman reported the decease of Professor J. H. van't Hoff, an Honorary Member of the Royal Institution, and a resolution of condolence with the family was passed.

THE WEIGHT OF A "NORMAL" LITRE OF HYDROGEN CHLORIDE AND THE ATOMIC WEIGHT OF CHLORINE.*

By FRANK PLAYFAIR BURT and R. W. WHYTLAW GRAY.

As the result of an exhaustive research on the density of hydrogen chloride, involving no fewer than twenty-eight weighings of the gas, Herr Otto Scheur (*Zeit. Phys. Chem.*, 1909, lxviii., 575) concludes that the weight of a normal litre is 1·63944 ± 0·00004 grms., and that the value 1·63915 ± 0·00005 grms. previously obtained by us is slightly too small (*Trans. Chem. Soc.*, 1909, xcv., 1644). The difference between the two values hardly exceeds 1 part in 6300, but is much greater than the mean probable error calculated for each series by the method of least squares, and in consequence the atomic weight of chlorine obtained by combining the density with the results of our volumetric analysis and compressibility measurement is affected by an uncertainty of the same order. Our values for chlorine are in striking agreement with those of Dixon and Edgar; those of Scheuer are slightly higher, but all three sets of results are very appreciably larger than the values found by Noyes and Weber (*Journ. Amer. Chem. Soc.*, 1908, xxx., 13), and by Richards and his colleagues (*Ibid.*, 1909, xxxi., 6).

The calculation of the most probable atomic weight to be assigned to this element is further complicated by the slight uncertainty which still exists in the atomic weight of hydrogen. According to Morley if O = 16 H = 1·00762 (*Zeit. Phys. Chem.*, 1896, xx., 1), whilst according to Noyes H = 1·00787 (*Journ. Amer. Chem. Soc.*, 1907, xxix., 1718). In consequence, some of our own results, and Scheuer's, as well as those of Dixon and Edgar (*Phil. Trans.*, 1905, ccv., 169), and Noyes and Weber, lead to two parallel sets of numbers, and it is difficult to say which mean value is the more exact approximation.

A choice between the two must clearly be governed by the results of other determinations in which chlorine has been referred more or less indirectly to oxygen; but apart from physico-chemical evidence there are only two investigations which fulfil these conditions, viz., that of Richard and his colleagues (*loc. cit.*), in which chlorine and oxygen were linked by means of the ratios Ag : $AgNO_3$, Ag : AgCl and AgCl : NH_4Cl, and that of Guye and Fluss (*Journ. Chim. Phys.*, 1908, vi., 732) who directly compared the atomic weights of nitrogen, oxygen, and chlorine by the analysis of nitrosyl chloride.

The two values yielded by these researches are :—

Richard	Cl = 35·456
Guye and Fluss	Cl = 35·466

Richards' value involves a knowledge of the atomic weights of hydrogen and nitrogen, but a slight variation in the former hardly affects the results, and there can be little doubt now that the uncertainty in the latter is very small (Guye and Drouginine, *Journ. Chim. Phys.*, 1910, viii., 473). The method of Guye and Fluss has the advantage of affording a direct comparison between chlorine and oxygen; but the agreement one naturally expects between the results of the two researches is strikingly absent, the values differing by nearly 1 part in 3500, so that no decisive conclusion can be drawn from this evidence.

Table I.—*The Atomic Weight of Chlorine*, O = 16.

	H = 1.0076	H = 1·00787.
Noyes and Weber	35·452	35·461
Gray and Burt	35·459	35·467
Edgar (*Phil. Trans.*, 1908, A, ccix., 1)	35·461	35·469
Edgar (*Ibid.*)	35·462	35·470
Dixon and Edgar	35·463	35·471
Scheuer	35·465	35·471
Mean	35·460	35·468

* A Paper read before the Faraday Society, March 14, 1911.

Physico-chemical measurements afford another means of obtaining the atomic weight of chlorine directly in terms of the oxygen standard. By comparing the limiting densities of oxygen and hydrogen chloride the molecular weight of the latter gas can be obtained. The atomic weight of the halogen can then be deduced by subtracting the atomic weight of hydrogen, which in this case does not need to be known with great exactness. This was the method we followed in the latter part of the research already cited, and we obtained for chlorine the value 35·461, but the substitution of Herr Scheuer's density for ours yields the value 35·466. It is true that the concordance here is greater than in the former case, but it can hardly be said to set at rest all doubts on the question at issue. A knowledge of the exact value of the density of hydrogen chloride is hence of great importance in a discussion of the true atomic weight of chlorine. At present there is no reason why the values of Dixon and Edgar, Edgar, ourselves, and Scheuer referred to the higher hydrogen basis, as well as that of Guye and Fluss, should be any less probable than the much lower value of Richards, and that of Noyes and Weber expressed on the lower hydrogen basis, but if the density of hydrogen chloride were established beyond doubt within narrow limits of error, strong evidence would be furnished in favour of one of the two competing sets of values.

Before attempting to decide which of the two values for the weight of a normal litre, our own or Scheuer's, is the closer approximation, it is necessary to consider the errors which may have affected both series of results.

Discusssion of the Chief Sources of Error in the Determination of the Density of HCl.

Our experience in measuring the density of this gas has been in many respects similar to Scheuer's. The individual results agree fairly well among themselves, but not so well as the errors of measurement would lead one to expect. The total probable uncertainty in each individual result is, in Scheuer's case, about 1 part in 5000; in our case it is of the same order, and yet the maximum deviations in the two cases are 1 part in 1640 and 1 part in 1533 respectively. This can harly be attributed to a vitiation in purity of the gas, for fractionation did not cause a progressive change in density, and, moreover, our volumetric analyses yielded very concordant values. We must therefore conclude that these variations are caused by some disturbing factors, which are inherent in the methods employed. Several possibilities are worthy of consideration, and the more important appear to us to be :—

(*a*) Chemical action of the gas on the lubricant used for the stopcocks.
(*b*) Solution of the gas in the lubricant.
(*c*) Adsorption of the gas on the glass surfaces of the density bulbs.

a and b.—It is probable that there is no stopcock lubricant which does not dissolve this gas to an appreciable extent. Our earlier experiments were carried out in an apparatus in which the stopcocks were lubricated with a grease compounded of the same ingredients as that used by Scheuer. We found the grease was markedly attacked by the gas, soon becoming dark in colour and in some cases apparently charring. This has also been noticed by Steele and Bagster (*Trans. Chem. Soc.*, 1910, lxc., 2608). Its use was therefore abandoned in favour of a pure paraffin lubricant, and the densities previously obtained were rejected. It is noteworthy that the mean of these densities agrees very closely with Scheuer's results, as Table II. shows, and is in marked contrast to our later mean, viz., 1·63922, obtained in the same bulb, when the rubber grease was replaced by the paraffin lubricant. Without laying too much stress on this point, we are inclined to believe that rubber vaseline grease is unsuitable for use with hydrogen chloride, and partially accounts for the discrepancy between Scheuer's results and our own,

TABLE II.—*Gas from* NH_4Cl *and Concentrated* H_2SO_4 *Rubber Grease on Taps.*

(Weight of a normal litre no correction for adsorption.)

	1·63958
	1·63921
	1·63927
	1·63987
	1·63986
	1·63936
Mean ..	1·63952

Even in presence of a lubricant which is not chemically attacked there is still the possibility of an appreciable error resulting from solution. The tap grease dissolves the gas, and part of this is given off when the density bulb is pumped out. In practice this effect will tend to make the density determinations too high. During the filling and adjustment of the temperature and pressure the grease partially saturates itself and causes the full bulb to weigh more than it should. On exhaustion all or part of the gas in solution is given up and the subsequent weighing approximates closely to the initial one, so that the non-variation in weight of the empty bulb during a series of determinations is no proof of the absence of this error. That solution actually occurs is proved both by Scheuer's results (*loc. cit.*, 1910, p. 601) and our own (*loc. cit.*, p. 1643), but the amount of gas dissolved or given up varies so much with the experimental conditions that it is not possible to apply a constant correction.

(*c*) *Adsorption.*—The adsorption or condensation of compressible gases on glass surfaces has often been pointed out as a source of error of uncertain magnitude in exact determinations. Most experimenters have sought to determine its influence by varying the capacity of the bulb in which the gas is weighed. This method has yielded no very definite results for gases beyond showing that the magnitude of the effect must be small (G. Baume, *Journ. Chim. Phys.*, 1908, vi, 1. Guye and Davila, *Mém. de la Soc. de Phys. et d'Hist. Nat. Genève*, 1908, xxxv., 635). It will generally be admitted that when a given mass of gas is introduced into a glass vessel the pressure exerted by the gas on the walls will, on account of adsorption, be slightly diminished. The greater the ratio of surface to volume the greater will be the diminution of pressure, and conversely the pressure corresponding to the total number of molecules in the mass of gas will only be reached when this ratio is infinitely small. As McBain (*Zeit. Phys. Chem.*, 1909, lxviii., 497) has shown in the case of hydrogen adsorbed by cocoa-nut charcoal, the total quantity of condensed gas exists in two states—(*a*) a surface film, (*b*) a solution in the material of the condensing surface. When equilibrium between the gas and its condensing surface has been obtained a constant fraction of the total mass of gas is present in these two states, but the magnitude of this fraction, surface remaining constant, must clearly depend on the concentration of the gas producing adsorption and also on the temperature. In other words, the actual mass adsorbed will vary with the pressure and temperature of the gas in the vessel.

In the case of hydrogen and charcoal, McBain has shown that equilibrium between the free gas and that adsorbed as a surface layer is quickly reached, whilst adjustment of equilibrium of the gas in solution proceeds slowly and is only complete after a considerable interval of time. Bearing in mind the possible existence of these two effects, we have investigated the adsorption of HCl on glass surfaces in the following way:—

The method, of which only a brief account has appeared before, was originated by a suggestion of Prof. W. Ostwald, and is based on the assumption that when gas is displaced a constant pressure from a glass vessel by means of mercury the adsorbed gas remains behind between the mercury and the glass surface, and can afterwards be collected by lowering the mercury so as to produce a Torricellian vacuum. The adsorbed gas given up is then removed, and the process can be repeated until further evolution ceases. The apparatus consisted of two cylinders A and B, of about 300 sq. cm. internal surface, connected with each other through a two-way stopcock C. The cylinders could be filled with mercury from the reservoirs D and E, which were attached to a cord running over the pulleys G and H. This system of adjustment enabled one to transfer the gas from one cylinder to the other at constant pressure. The cylinder B was not used in the measurements, and merely served as a reservoir for the collection of the displaced gas.

The measuring cylinder A was surrounded with ice and water contained in a tin bath, and the capillary tube K, which was carefully calibrated, was used for the measurement of the volume of the adsorbed gas.

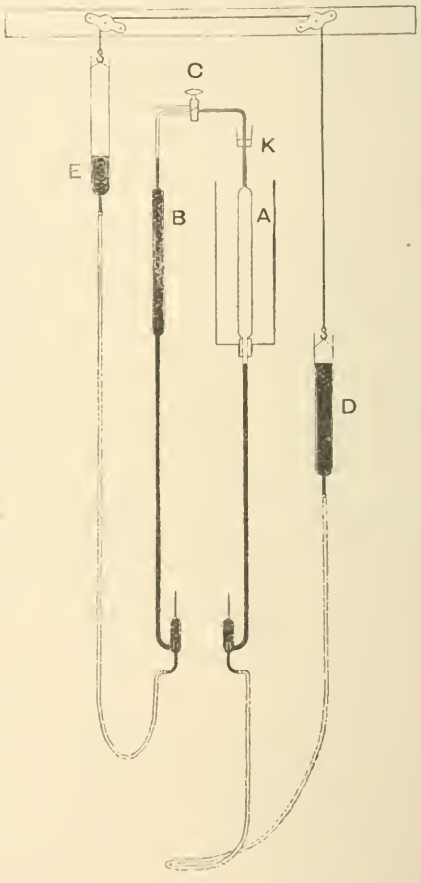


FIG. 1.

Before the hydrogen chloride entered the apparatus the greatest care was taken to ensure the complete absence of moisture, for both Scheuer and ourselves found that condensation is greatly increased if the vessels are not thoroughly dry. The gas was left in contact with the glass for twenty-four hours, and then displaced into the cylinder B at constant pressure. The tap C was then turned off, and a short length of the mercury thread was frozen in the calibrated capillary by means of solid carbon dioxide contained in the paper vessel L. This was necessary because the gas dissolved in the grease of the tap, and afterwards slowly evolved in a vacuum. The mercury was next lowered so as to produce a vacuum, into which the adsorbed gas escaped, and on allowing mercury

to refill the cylinder this gas was collected and measured, and afterwards removed through the tap C. This series of operations was repeated a number of times, allowing definite intervals for the adsorbed gas to accumulate in the vacuum, until the volume obtained became negligibly small. The increments of gas were summed, and in this way the total gas volume given off from the walls of the cylinder in a given time was obtained. Cylinder A was allowed to saturate itself with gas at four different initial pressures. The results are given in Table III.

Table III.

Pressure during saturation.	Volume of gas at normal temperature pressure in c.c.	Time of exposure of walls to vacuum in minutes.
730	0·0086	33
730	0·0098	136
730	0·0103	246
547	0·0055	31
547	0·0067	188
547	0·0070	279
317	0·0038	31
317	0·0047	130
317	0·0048	217
218	0·0028	32
218	0·0033	110

appreciable fraction continues to be given off at a gradually decreasing rate, which does not reach zero even after five hours. Thus at a saturation pressure of 732 mm. 0·0086 cc. is given off after thirty-three minutes, and only 0·0018 cc. more is yielded after five hours. The quantity of gas condensed is very nearly directly proportional to the pressure, and lends no support to the view of Scheuer that the adsorbed layer is permanent, and does not vary with the degree of evacuation of the bulb. Very similar curves to ours have been obtained by McBain in the research already cited, so that it is legitimate to conclude that our results establish for HCl on glass surfaces the existence of the two kinds of adsorption. From these curves the total quantity of gas adsorbed per sq. cm. surface at a saturation pressure of 760 mm. after equilibrium has been obtained can be calculated if the adsorption be assumed to be directly proportional to the saturation pressure. This is for the glass of the cylinders 0·036 cub. mm. at 0° and 760 mm., for the the glass of the moulded bulb 0·146 cub. mm. at 0 and 760 mm. The adsorption, even on the surface of the moulded bulb, is hence very small, and need only be taken into account when results of the highest degree of accuracy are desired. The actual adsorption on the glass density bulb itself was not measured, but experiments in a similar bulb showed that it approximated to the higher figure, and the correction applied in

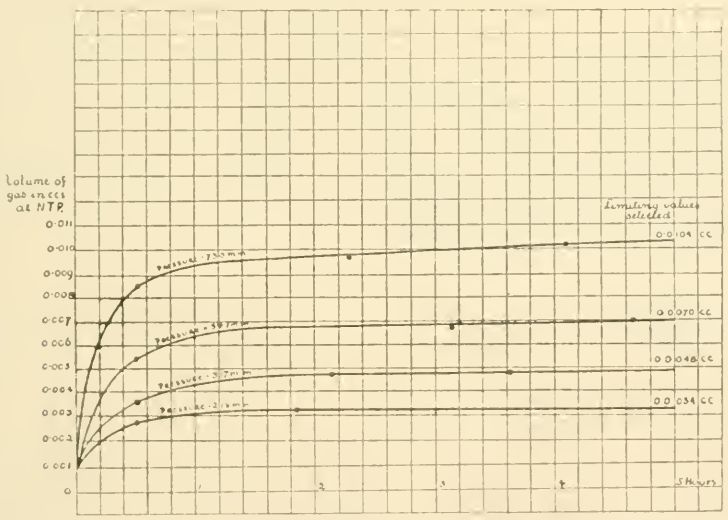


Fig. 2.—Hydrogen Chloride Adsorption Curves, Glass Cylinder 300 sq. cm.; Temp. 0° C.

The volumes of gas evolved were then plotted against the times of exposure to vacuum, and yielded a series of four curves, which are here reproduced (Fig. 2).

In addition, the total adsorption was measured on a different glass surface by replacing cylinder A by a thick-walled bulb of moulded glass. The volume of gas condensed was in this case considerably larger, being 0·047 c.c. at normal temperature pressure for a surface of 320 cm. for a saturation pressure of 782 mm. It might be supposed that part of the gas set free in this way had been mechanically imprisoned in cavities in the glass by the rising mercury. To test this point similar experiments were carried out on air and also on hydrogen. The volume of air adsorbed was very much smaller, but curves of exactly the same type resulted.

The adsorption with hydrogen was barely detectable. Had the gas been mechanically imprisoned the volume of air or hydrogen should have been of the same order of magnitude as that of the hydrogen chloride.

The form of the curves shows that the larger portion of the condensed gas is very quickly evolved *in vacuo*. An our previous research was calculated from this. Objection to the correction might be taken on the ground that it is smaller than the probable experimental error of each individual determination. The probable accuracy of the mean of a series of values is, however, very much greater, and since an error of known magnitude is introduced by adsorption, the correction seemed to us legitimate. Our glass density bulb had an internal surface of 291 sq. cm. The correction per litre is hence 0·00014 grm., which only changes the density by one part in 10,300. It is, however, to be noted that a very small trace of moisture on the glass surfaces of the bulb would increase greatly the magnitude of this correction.

With regard to the sign of the adsorption correction, we find ourselves totally at variance with Scheuer (*loc. cit.*, p. 613). Our results prove conclusively the adsorbed layer of gas is not of constant mass, and varies with the pressure in the density bulb, temperature remaining constant. In consequence the apparent density, whether determined by the method of Regnault or by the charcoal adsorption method, will be, in all cases, slightly too large, and must be

decreased by the weight of the adsorbed gas. It is true that the adsorbed gas is not evolved immediately on evacuating the density bulb, but in our experiments the latter was exposed to low pressure for at least two hours during the adsorption by cocoa-nut charcoal, and it is easily seen from our curves that the residual gas must have been of quite negligible mass. This was confirmed by direct experiments in which the exhausted bulb was washed out with silver nitrate solution (*Trans. Chem. Soc., loc. cit.*).

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 23rd, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Theory of Asymptotic Series.*" By G. N. WATSON, M.A., Fellow of Trinity College, Cambridge.

"*Ionisation of Heavy Gases by X-Rays.*" By R. T. BEATTY.

"*Variation of the Ionisation with Velocity for the β-particles.*" By W. WILSON, M.Sc.

Rays of different speeds were separated, by means of a magnetic field, from the heterogeneous beam given out by the active deposit from radium.

The relative numbers of particles corresponding to the different speeds were determined by measuring the charges gained per second by an insulated copper vessel which was placed in the path of the rays and was thick enough to completely absorb them. The corresponding ionisations were determined by a separate experiment, and were corrected for scattering of the rays by the walls of the ionisation vessel.

The results obtained are as follows:—

(1) The ionisation produced per cm. by β-particles in free air varies inversely as the square of the velocity between the limits examined.

(2) The ionisation in a thick copper vessel is not connected with the velocity by any simple law, but can be approximately represented by $I = k(c - v)$, where I is the ionisation, v the velocity of the particles, and k and c constants.

"*Causes of Absorption of Oxygen by the Lungs in Man.*" By C. G. DOUGLAS and Dr. J. S. HALDANE, F.R.S.

"*Influence of Planets on the Formation of Sun-spots.*" By ARTHUR SCHUSTER, F.R.S.

In this investigation the relative position in heliocentric longitude of a planet, and that point of the sun's disc where a spot is first observed, is taken as starting-point. Spots first noticed within 60° of the eastern limb were excluded on account of the possibility or probability that these spots were formed in the invisible hemisphere and only brought into view by the rotation. The total number of spots taken into account was about 4250. Imagine an observer placed on the sun. He might observe within each solar rotation, imagined to be divided into twenty-four hours, a planet rising, reaching a maximum altitude, called "planetary noon," descending and setting.

The chief results of the investigation, dealing with the planets Mercury, Venus, and Jupiter, are as follows:—

1. More spots are formed when the planet is above the horizon than during the planetary night. The excess amounts to 4·5 per cent in the case of Mercury, 6·4 per cent in the case of Venus, and 1·5 per cent in the case of Jupiter. The probability that this excess is accidental in the case of Mercury and Venus is about 1 in 7 and 1 in 17 respectively. In the case of Jupiter the difference is no more than might be expected by the theory of chance. Not much importance is attached to each of these results taken separately, but if the theory of probability be applied to the combined results, an accidental coincidence of the excesses of one hemisphere over the other to the amounts indicated will not happen more than once in 1150 cases.

2. More decided results are obtained if the formation of spots during different parts of the planetary day are investigated. If the distribution were purely accidental, twice as many spots should form during the eight hours after the planet has risen as in the four hours before it sets. It is found on the contrary that during the latter interval the number of spots bears a proportion of 0·344, 0·349, and 0·347 respectively to the whole instead of 0·333, the planets always being taken in order of distance from sun. The average excess here amounts to about 5 per cent.

3. The effect of the planets when compared in detail exhibits remarkable similarities. At an observing station on the sun, a strong minimum of spot formation is found to exist shortly before the planet rises; this is followed by a decided maximum in all three cases one hour after the rise. This is succeeded by a drop in activity, leading to a minimum, which occurs sooner with Mercury and Venus than with Jupiter, but this distinction may be accidental. The most remarkable feature in all three cases is the rapid rise from a secondary minimum, one hour after the planetary noon, to a pronounced maximum two hours later. This is followed by a drop lasting until the hour before the planet sets. The action after that and during the greater part of the planetary night is irregular, and might disappear if a larger quantity of material were available. The probability that all three planets should show their greatest activity at the same hour to the extent shown by the figures is one part in 130 million. The probability of the corresponding minimum in the planetary morning is not much less, so that taking the coincidence of both these factors into account, we may exclude the possibility of an accidental coincidence.

CHEMICAL SOCIETY.

Ordinary Meeting, March 16th, 1911.

Prof. HAROLD B. DIXON, M.A., Ph.D., F.R.S., President, in the Chair.

THE PRESIDENT referred to the death of Geheimrath Prof. Dr. Jacobus Heinricus van 't Hoff (elected an Honorary and Foreign Member of the Society on February 2nd, 1888), who died on March 1st last. He stated that the following telegram had been sent to Frau van 't Hoff in the name of the Society:—

"The President, Officers, and Council of the Chemical Society deeply mourn the loss of their distinguished Honorary and Foreign Member, Professor Doctor J. H. van 't Hoff."

Messrs. Harold J. Page and F. Challenger were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Ernest Carr Bennison, 4, Sir John's Road, Selly Park, Birmingham; Richard Charles Bowden, B.Sc., 21, Rokeby Avenue, Redland, Bristol; Algernon John Elkington, 26, Rye Hill Park, S.E.; Alfred Walker Empson, 174, Dhunumtollah Street, Calcutta; Idris Larkby Owen, M.Sc., 101, Flover Road, Small Heath, Birmingham; Robert Robison, Ph.D., B.Sc., 227, Woodborough Road, Nottingham.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. John Ernest Roux Adendorff, Randfontein, Transvaal; Atulchandra Datta, M.A., Bag Mozaffar Khan, Agra; Thomas Grantham Giddy, High Street, Newcastle, N.S.W,

A proposal having been made by some of the old students of Robert Wilhelm Bunsen to send a wreath to place at the foot of his statue in Heidelberg on the occasion of the one-hundredth anniversary of his birth (March 31st), the President stated that the Council had authorised him to sign, on behalf of the Chemical Society, the inscription attached to the wreath.

The President read a letter addressed to the Council by Sir Edward Thorpe, stating that a committee had been formed with the object of raising a fund for the erection of a memorial to Joseph Priestley in his native town of Birstall, Yorkshire.

Subscriptions to the fund should be sent to Mr. W. Bagshaw, at Moorfields, Birkenshaw, Leeds.

Of the following papers those marked * were read :—

*69. "*Apparatus for the Maintenance of Constant Pressures above and below the Atmospheric Pressure. Application to Fractional Distillation.*" By John Wade and Richard William Merriman.

For pressures below the atmospheric pressure, air is exhausted continuously from the system by an ordinary water-pump. For pressures above the atmospheric pressure, air or other gas is forced in continuously by an automatic compressor, actuated by falling mercury. The pressure is kept constant by a regulator or compensator consisting of an open syphon manometer, which allows air or other gas to escape from, or enter, the system as soon as the desired excess or diminution of pressure is exceeded.

Various devices were also described in connection with fractional distillation, more especially for changing the receiver without disturbing the pressure.

Discussion.

The President recalled the simple method used by Prof. F. D. Brown twenty-five years ago for distillations under reduced pressure. The apparatus devised by the authors was obviously an instrument of great delicacy. He also congratulated the authors on having devised a convenient apparatus for keeping up a high-pressure supply of gases in which the pressure was automatically regulated. He would have found such an apparatus of great use in his work on the ignition-points of gases at varying pressures.

Dr. Forster inquired as to the experience of the authors in connection with bumping. At the lower pressures referred to by Dr. Wade, bumping would present much inconvenience unless checked by admission of air, and as it was the speaker's experience that under very low pressures liquids distilled without bumping, he was interested to know whether this phenomenon accompanied distillation under pressures much exceeding one atmosphere.

Dr. Wade said that he and his colleague had experienced no difficulty with bumping ; the liquids so far investigated boiled under pressures above atmospheric with perfect steadiness. The only difficulty encountered under high pressures was the great increase in the amount of air dissolved in the distillate, which escaped with considerable energy on releasing the pressure. He thought that Dr. Forster's suggestion of distilling volatile liquids under increased pressure in order to avoid bumping was eminently practicable.

*70. "*The Influence of Water on the Boiling-point of Ethyl Alcohol at Pressures above and below the Atmospheric Pressure.*" By John Wade and Richard William Merriman.

The ratio of water to alcohol in the binary mixture of minimum boiling-point, isolated by Young and Fortey (*Trans.*, 1902, lxxxi., 1717) by systematic fractional distillation, is increased by raising, and diminished by lowering, the pressure under which the fractionation is effected. At pressures below about 80 mm., corresponding with temperatures below about 25°, ethyl alcohol and water cease to form a binary mixture. Under these conditions, anhydrous alcohol is the most volatile phase present in ordinary spirit, and may be separated from the water to any desired extent by systematic fractional distillation. For the same reason, although alcohol, contrary to general belief, is not appreciably hygroscopic, the percentage of water in moist alcohol is slowly increased by exposing it to air, or even by passing dry air through it.

*71. "*The Interaction of Aromatic Disulphides and Sulphuric Acid.*" By William George Prescott and Samuel Smiles.

When the solutions of certain disulphides in sulphuric acid are mixed with simple aromatic compounds, sulphurous acid is evolved, and unsymmetrical monosulphides are formed. Reasons were adduced in support of the hypothesis that preliminary fission of the dithio-system is effected by the acid, the sulphoxylic acid and mercaptan being produced :—

$$\text{i. } Ar{\cdot}S{\cdot}S{\cdot}Ar + H_2O \rightarrow Ar{\cdot}S{\cdot}OH + ArSH.$$

The first-named substance then yields the unsymmetrical monosulphide by condensation with the aromatic compound—

$$\text{ii. } Ar{\cdot}S{\cdot}OH + HAr' = Ar{\cdot}S{\cdot}Ar' + H_2O,$$

whilst the mercaptan is oxidised to the disulphide (Stenhouse, *Annalen*, 1869, cxlix., 250), which is then available for renewed decomposition. It was further shown that the character of this reaction (i.) strongly suggests that it is reversible.

This hypothesis explains and correlates in a simple manner all the known reactions of disulphides and mercaptans in sulphuric acid.

*72. "*The Absorption Spectra of Permanganates in certain Solvents.*" By Thomas Ralph Merton.

Measurements have been made of the three least refrangible bands in the absorption spectra of potassium, calcium, barium, and zinc permanganates, in water, acetone, acetic anhydride, acetonitrile, methyl acetate, pyridine, methyl alcohol, ethyl alcohol, and ethylene glycol, except in those cases where the reaction between the salt and the solvent is too rapid for measurements to be made; the positions of the absorption maxima vary in different solvents, although the general character of the absorption remains the same.

Discussion.

Dr. Merton stated, in reply to a question, that no steps had been taken to secure large crystals of the solid solution, as this was not necessary for the purpose of observing the absorption spectrum.

*73. "*The Resolution of Asymmetrical Derivatives of Phosphoric Acid.*" By Frederick Stanley Kipping and Frederick Challenger.

This work is a continuation of that published by Luff and Kipping (*Trans.*, 1909, xcv., 1993), and deals with the preparation and resolution of dl-*phenyl-β-naphthyl hydrogen phosphate*, $PO(OPh)(O{\cdot}C_{10}H_7){\cdot}OH$.

Attempts to resolve this acid by the fractional crystallisation of the salts which it forms with optically active bases were unsuccessful, but the l-*menthylamide*, $PO(OPh)(O{\cdot}C_{10}H_7){\cdot}NH{\cdot}C_{10}H_{19}$, was easily separated into its stereochemically isomeric components.

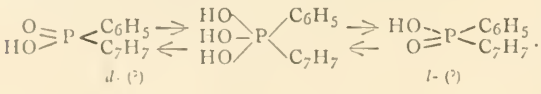
Discussion.

Prof. Frankland asked what was the order of the difference in rotation of the two isomeric menthylamides. He suggested that the hydrolysis of the menthylamides might probably have been effected if hydrochloric acid instead of potash had been used. He also thought that the resolution of the acid might have been more advantageously attempted by adopting McKenzie's method of partial esterification with menthol or some other optically active alcohol, and that similarly the acid chloride might have been made to interact with an insufficient quantity of an optically active primary or secondary amine.

Dr. Lowry agreed with the authors that the isomeric amides could not be—

$$(3 \text{ and } 4)O \gtrless P < \begin{matrix} C_6H_5(1) \\ C_7H_7(2) \end{matrix} \quad \text{and} \quad (3)HO \gtrless P < \begin{matrix} C_6H_5(1) \\ C_7H_7(2) \end{matrix}$$
$$(5)NHX \qquad\qquad (4 \text{ and } 5)NX$$

since such compounds would certainly be interconvertible. The production by a reversible action of a mere trace of one of them would, further, be sufficient to bring about the inversion or racemisation of the *d*- and *l*-forms of the other; the double bond of the first compound could be broken in such a way as to produce the OH in position 3 or 4, whilst the breaking of the double bond of the second compound could give rise to NHX in position 4 or 5; the linkings 3, 4, and 5 would, therefore, be interchangeable, and optical activity could not be expected to persist. In the case of the acids, which had resisted all attempts at resolution, it was probably impossible to isolate *d*- and *l*-forms; the addition and removal of water afforded a mechanism for interchanging the linkings in ways that would almost certainly result in optical inversion and consequent racemisation.



d- (?) *l*- (?)

74. "*The Action of Carbon Dioxide in the Bleaching Process.*" By SYDNEY HERBERT HIGGINS.

On adding calcium chloride to lime-water, the rate of attraction of carbon dioxide from the air by the lime-water is increased, and this fact probably accounts for the observation that the addition of calcium chloride to bleaching powder solution increases the bleaching efficiency of that solution. On exposing bleaching powder solution to air, the free lime contained in the solution is deposited as calcium carbonate, and then the carbon dioxide of the air acts on the other calcium salts present in solution. It is the latter action that causes the exposed bleaching powder solution to have a high bleaching efficiency. Common salt added to sodium hypochlorite solution increases its bleaching activity, and this is also true of other neutral salts of sodium; solutions containing equivalent proportions of these salts have approximately the same effect in increasing the bleaching activity. Moreover, equivalent proportions of common salt and of calcium chloride have approximately the same effect in increasing the activity of bleaching powder solutions. These effects are probably due to the so-called "neutral salt action" and to the increased attraction of the carbon dioxide of the air by the neutralt salt solutions. The results of the experiments and other facts (Higgins, *Journ. Soc. Chem. Ind.*, 1911, xxx., 185) do not agree with the conclusions of Taylor (*Trans.*, 1910, xcvii., 2541). The author represents the action of carbon dioxide on bleaching powder by the following equations:—

(1) $Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2HOCl.$
(2) $2HOCl + CaCl_2 + CO_2 = CaCO_3 + 2Cl_2 + H_2O.$

The action represented by equation (2) is found to be reversible, and thus accounts for Taylor's (*loc. cit.*) and the author's results. In bleaching with bleaching-powder solution, hypochlorous acid enters into the bleaching action, and as much nascent chlorine as is supplied by the reaction represented in equation (2), the carbon dioxide being supplied by the air.

75. "*The Relation between the Absorption Spectra of Metallic Ions and their Valency.*" (Preliminary Note). By CECIL REGINALD CRYMBLE.

A study is being made of the absorption of light by aqueous solutions of the salts of metals.

A metallic ion is regarded as being "non-absorptive" when 10 mm. of a normal solution of its salt, or a length of solution containing an equivalent amount of the metal, transmits the spectrum of the iron arc up to λ 2300.

In photographing the absorption spectra, solutions of salts of the metals, such as chlorides or sulphates, have been employed, as in these cases the acidic radicle is non-absorptive, and the absorption, if any, must be due to the metal.

The metals that have been examined up to the present may be grouped into two classes, namely, "non-absorptive" and "absorptive."

The first class, "non-absorptive," contains the following metals:—

Li, Na, K, Gl, Mg, Zn, Cd, Ba, Al, Th.

The second class, "absorptive," contains:—

Metals giving colourless solutions Hg, Tl, Sn, Pb, Sb, B^{i}
Metals giving coloured solutions Cu, Ce, Mn, Fe

In addition to the metals giving coloured ions, the following metals give coloured solutions, and may be included under that head:—

Au, Cr, U, Co, Pt, Ti, V.

When regarded from the point of view of valency, it will be observed that the first-class comprises the metals of constant valency, that is, the metals which are incapable of giving two series of salts, and that the second class comprises the metals of varying valency, that is, those metals which give two or more series of salts—the valency of a metal being determined by the fluorine or chlorine compounds which it forms.

The metals which give absorptive ions may be divided into those showing selective absorption, such as—

Cu, Ce, Cr, Mn, Fe, Co,

and those showing general absorption only, like—

Tl, Sn, Pb, Sb.

The former give two series of salts in which the metal, in passing from the "ous" to the "ic" form, increases its valency by one; for example, iron gives the chlorides $FeCl_2$ and $FeCl_3$.

In the latter group the metal, when changing from the state of low valency to that of high valency, increases its valency by two; for example, tin gives the chlorides $SnCl_2$ and $SnCl_4$.

It has not yet been determined, however, whether this relation is present in all cases.

The research is being continued with a view to observing the difference in absorptive power between the two forms of the same metal where the metal gives two series of salts, and to investigating the absorption spectra of the metalloids and non-metals. An attempt is also being made to trace a relationship between the absorption spectra of the metallic ion and the position of the metal in the electro-potential series.

76. "*The Elements* Cu | Cu_2O *Alkali* | H_2 *at* 0°." By ARTHUR JOHN ALLMAND.

The electrode system Cu | Cu_2O—N-NaOH was measured at 0°, and by combining with it the calculated value for the electrode H_2 | N-NaOH, the value of the E.M.F. of the cell Cu | Cu_2O alkali | H_2 at 0° was obtained. It is one centivolt higher than the value calculated by Nernst's theorem.

77. "*A Standard Electrode with Alkaline Electrolyte*: Hg | HgO *Alkali*." By FREDERICK GEORGE DONNAN and ARTHUR JOHN ALLMAND.

The authors have extended previous work carried out with this system, and have been able closely to define three standard electrodes at 25° and 0°, namely:—

Hg | HgO N-KOH.
Hg | HgO N-NaOH.
Hg | HgO N/10-NaOH.

The mean errors of the values given vary between ±0·00002 and ±0·00011 volt.

78. "*The Volatile Constituents of Coal.*" Part II. By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

In continuation of their previous work, the authors have studied the action of heat on coal, paying particular attention to the composition of the gases evolved during successive stages of distillation at a uniform temperature. They find that coal contains two types of compounds of different degrees of ease of decomposition. The one, the

more unstable, yields the paraffin hydrocarbons and no hydrogen; the other, decomposed with greater difficulty, yields hydrogen alone (or, possibly, hydrogen and the oxides of carbon) as its gaseous decomposition product. The authors consider that the difference between one coal and another is determined mainly by the proportions in which these two types of compounds exist; and that the true "coal substance," apart from the traces of sulphur compounds and other substances which mask its character, is compounded of the two types that behave so differently under the action of heat. It has been shown that there is considerable justification in assuming that one type of compound in coal, the vegetable origin of which is undoubted, is a degradation product of cellulose. The authors identify the "hydrogen-yielding constituents" with this type, and regard the "paraffin-yielding constituents" as being most probably derived from the resins and gums originally contained in the sap of the coal plants. They suggest that the substance which P. P. Bedson (*Journ. Soc. Chem. Ind.*, 1908, xxvii., 147) has shown to be extracted in considerable quantity from coal by the solvent action of pyridine is compounded of the "paraffin-yielding constituents"; and they therefore regard coal as a conglomerate of which the degradation products of cellulose form the base, and the changed resins and gums of the coal plants the cement.

79. "*The Absorption Spectra of Chlorobenzene and Bromobenzene as Vapours, as Liquids, and in Solution.*" By JOHN EDWARD PURVIS.

The chief results of the investigation are—(1) that the vapours of chloro- and bromo-benzene exhibit a considerable number of narrow bands which can be divided into groups; (2) that alcoholic solutions exhibit seven diffuse bands which are comparable in appearance, and only differ in their relative positions; (3) that very thin films exhibit seven diffuse bands which are comparable with each other and with the bands of the solutions, and only differ in their relative positions.

80. "*Orthophosphoric Acid as a Dehydrating Catalytic Agent.* Part I. *The Condensation of Acetone in presence of Phosphoric Acid.*" By PANCHANAN NEOGI.

The author finds that in presence of ortho- and meta-phosphoric acids, acetone condenses to form mesitylene, mesityl oxide, phorone, and xylitone. A given quantity of the acid has repeatedly been used to convert fresh quantities of acetone into its condensation products.

81. "*Trialkylammonium Nitrites and Nitrites of the Bases of the Pyridine and Quinoline Series.*" (Part I.). By PANCHANAN NEOGI.

Triethylammonium nitrite and *pyridinium nitrite* have been prepared by the interaction of silver nitrite and the hydrochlorides of the bases. The former exists both in monohydrated and anhydrous conditions, and can be sublimed unchanged under the ordinary, or under diminished, pressure. The latter is anhydrous, and is unstable.

82. "*Nitrites of the Alkylammonium Bases: Ethylammonium Nitrite, Dimethylammonium Nitrite, and Trimethylammonium Nitrite.*" (Preliminary Note.) By PRAFULLA CHANDRA RAY and JITENDRA NATH RAKSHIT.

In continuation of their previous work on methylammonium nitrite, the authors have succeeded in preparing the above members of the series by the same method, namely, interaction of silver nitrite and the corresponding chlorides of the alkylammonium bases and evaporation of the filtrate in a vacuum over sulphuric acid. Double decomposition between mercuric nitrite and the free bases in aqueous solution also furnishes the above products. It is worthy of note that whilst methylammonium nitrite is a yellowish-green crystalline substance, its homologue, *ethylammonium nitrite*, $NH_3Et{\cdot}NO_2$, is a viscid liquid of a pale brownish-yellow colour. *Dimethylammonium nitrite*, $NH_2Me_2{\cdot}NO_2$, is a limpid, pale yellow liquid. *Trimethylammonium nitrite*, $NHMe_3{\cdot}NO_2$, on the other hand, is a pale green crystalline solid.

83. "*Isomeric Monothiophosphates.*" By WILLIAM GIDLEY EMMETT and HUMPHREY OWEN JONES.

The isomeric α- and β-methyl monothiophosphates, $PS(OMe)_3$ and $PO(OMe)_2{\cdot}SMe$, have been examined in the hope that on saponification they would yield isomeric sodium monothiophosphates. Two different sodium dimethyl monothiophosphates are formed by the action of sodium methoxide on the esters, and a disodium methyl α-thiophosphate was obtained by saponification of the α-ester with sodium hydrosulphide, but no isomeric trisodium thiophosphates have been isolated.

The interactions of the esters and their derivatives with metallic salts have been examined.

Both α- and β-esters react with methyl iodide to give trimethylsulphonium iodide and a methyl phosphate.

84. "*The Absorption Spectra of Chlorobenzene, the Dichlorobenzenes, and the Chlorotoluenes.*" By EDWARD CHARLES CYRIL BALY.

The absorption spectra of chlorobenzene, the three dichlorobenzenes, and the chlorotoluenes have been observed with more efficient apparatus than was possible in the earlier work (*Trans.*, 1905, lxxxvii., 1332, 1355), Some new absorption bands have been detected.

85. "*Chemical Constitution and Hypnotic Action. Acid Amides and Products of the Condensation of Malonamides and Malonic Esters.*" By FREDERIC GEORGE PERCY REMFRY.

Acid amides are known to possess hypnotic properties to a certain extent. A number of compounds were prepared, in which one hydrogen atom of the amido-group was replaced by various radicles in the hope of increasing the hypnotic power of the acid amide. Such substances as *cinnamoyl*-p-*aminoacetophenone* (m. p. 204—205°), *dicinnamoylcarbamide* (m. p. 246°), and *α-bromoisovaleryl*-p-*aminoacetophenone* (m. p. 113—114°) in which both the acid amide and the substituent, when uncombined, have some narcotic properties, were found to be quite inactive. By condensing ethyl malonate with malonamide, *malonylmalonamide*,

$$CH_2<\begin{matrix}CO{\cdot}NH{\cdot}CO\\CO{\cdot}NH{\cdot}CO\end{matrix}>CH_2$$

(m. p. 252—253°), was obtained. Two alkyl groups can be attached to one of the "quaternary" carbon atoms and one to the other; the product, however, although somewhat resembling diethylbarbituric acid, a very strong hypnotic, was quite inactive. It was found that when a monoalkylmalonamide was condensed with ethyl malonate or ethyl alkylmalonate, a diketotetrahydropyrimidine was formed of the type $CR<\begin{matrix}N-CO\\NH{\cdot}CO\end{matrix}>CHR$. Ethyl monoalkylmalonates, ethyl dimethyl- and methylethyl-malonates (in part) condensed with malonamide to the eight-membered ring as above, but ethyl methylethylmalonate (in part) and the higher dialkylmalonates give a different condensation product with malonamide, the empirical formulæ of which alone have been determined. None of these compounds was physiologically active, nor was *ethylene*-bis-5-*propylbarbituric acid*—

$$CO<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}>C(C_3H_7){\cdot}CH_2{\cdot}CH_2{\cdot}C(C_3H_7)<\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}>CO$$

(which does not melt at 300°). *Dialkylmalonylbenzidines* of the type $CR_2<\begin{matrix}CO{\cdot}NH{\cdot}C_6H_4\\|\\CO{\cdot}NH{\cdot}C_6H_4\end{matrix}$ were too insoluble to be of any use, whilst *isobutyl allophanate*, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO_2{\cdot}CH_2{\cdot}CHMe_2$ (m. p. 178—179°), and *tert.*-amyl allophanate, $NH_2{\cdot}CO{\cdot}NH{\cdot}CO_2{\cdot}CEtMe_2$ (m. p. 151—152°), were inactive, the hypnotic properties of the respective alcohols being completely neutralised when combined with allophanic acid.

86. "p-*Benzoyloxybenzaldehyde*." By Frank George Pope.

The benzoyl derivative of *p*-hydroxybenzaldehyde was prepared in 1893 by Kopp (*Annalen*, cclxxvii., 350) by means of the Schotten-Baumann reaction in 10 per cent potassium hydroxide solution. The melting-point of the compound as obtained in this manner is given as 72°. Since an alkalihydroxide solution of such concentration might possibly affect the course of the reaction, it seemed better to carry out the operation in pyridine solution, and consequently 12 grms. of the aldehyde were dissolved in 30 cc. of pyridine and 14 grms. of benzoyl chloride added to the solution. The mixture was well shaken for half-an-hour, and then poured into 300 cc. of water, the precipitate collected, well washed, and crystallised from alcohol, when it separated in small colourless needles, melting sharply at 95°.

As such a considerable difference was found in the melting-points, a second preparation was made, using N-potassium hydroxide solution. The re-crystallised product in this case was also found to melt at 95°, and a mixture of the two specimens melted at 93°. Kopp's specimen thus seems to have been impure, and a few derivatives were therefore prepared in order to characterise the substance. *p*-Benzoyloxybenzaldehyde yielded the following numbers on analysis:—

0·1110 gave 0·3026 CO_2 and 0·0480 H_2O. C = 74·35; H = 4·80.

$C_{14}H_{10}O_3$ requires C = 74·34 H = 4·43 per cent.

The *oxime*, prepared in alcoholic solution, crystallised from dilute alcohol in brilliant colourless needles, melting at 129°:—

0·1190 gave 0·3034 CO_2 and 0·050 H_2O. C = 69·51; H = 4·62

0·1932 gave 10·2 cc. N_2 (dry) at 22° and 752 mm. N = 5·93

$C_{14}H_{11}O_3N$ requires C = 69·71; H = 4·57; N = 5·81 per cent.

p-*Benzoyloxybenzonitrile*, $C_6H_5{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CN$, was obtained by boiling 5 grms. of the oxime with 25 grms. of acetic anhydride under reflux for two hours. The product was poured, with continual stirring, into 500 cc. of water, when it set to a solid mass. This was collected, washed, and finally crystallised from dilute alcohol, from which it separates in colourless needles, melting at 95°:—

0·1304 gave 0·3610 CO_2 and 0·0476 H_2O. C = 75·70; H = 4·06

0·2452 gave 13·6 cc. N_2 (dry) at 18° and 752 mm. N = 6·39

$C_{14}H_9O_2N$ requires C = 75·34; H = 4·04; N = 6·44 per cent.

p-*Benzoyloxybenzaldehydephenylhydrazone*, prepared in glacial acetic acid solution, crystallises from alcohol, in which it is sparingly soluble, in colourless needles, melting at 178°:—

0·1016 gave 0·2830 CO_2 and 0·046 H_2O. C = 75·95; H = 5·03.

0·1038 gave 8 cc. N_2 (dry) at 18° and 754 mm. N = 8·97.

$C_{20}H_{16}O_2N_2$ requires C = 75·94; H = 5·06; N = 8·86 per cent.

The p-*nitrophenylhydrazone*, obtained in a similar manner, crystallises from hot glacial acetic acid, in which it is sparingly soluble, in small yellow plates, melting at 208°:—

0·1024 gave 0·2490 CO_2 and 0·0378 H_2O. C = 66·32; H = 4·10.

0·1046 gave 10·6 cc. N_2 (dry) at 18° and 754 mm. N = 11·78.

$C_{20}H_{15}O_4N_3$ requires C = 66·48; H = 4·15; N = 11·63 per cent.

p-*Benzoyloxybenzylidene*-p-*nitroaniline* was prepared by mixing alcoholic solutions of equivalent quantities of *p*-benzoyloxybenzaldehyde and *p*-nitroaniline. After some time a mass of yellow crystals separated, which were collected and re-crystallised from xylene; the substance separated as a felted mass of sulphur-yellow needles, melting at 199°:—

0·1322 gave 0·3366 CO_2 and 0·0476 H_2O. C = 69·44; H = 4·00.

0·1468 gave 10·4 cc. N_2 (dry) at 18° and 754 mm. N = 8·24.

$C_{20}H_{14}N_2O_4$ requires C = 69·36; H = 4·05; N = 8·09 per cent.

CORRESPONDENCE.

A CORRECTION.

To the Editor of the Chemical News.

Sir,—On behalf of our client Dr. Cain, the Editor of the *Journal of the Chemical Society*, we beg to draw your attention to an error on page 146 of your issue of the 31st March.

Professor Armstrong gives what purports to be a quotation from a telegram received by him from our client. The first word on the third line "letter" should read "latter term."—Yours, &c.,

Harford and Harford.

King's House,
33 and 37, King Street, Cheapside,
London, E.C., April 1, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Atti della Reale Accademia dei Lincei.
Vol. xx., No. 1, 1911.

Complex Molybdates of the Rare Earths.—G. A. Barbieri.—In a previous paper the author has described the preparation of an ammonium cero-molybdate, $(NH_4)_3Ce'''Mo_7O_{24}.12H_2O$, and of an ammonium lanthano-molybdate, $(NH_4)_3LaMo_7O_{24}.12H_2O$. He has now prepared by analogous methods the complex molybdates of the other elements of the cerium group, *i.e.*—

$(NH_4)_3PrMo_7O_{24}.12H_2O$
$(NH_4)_3NdMo_7O_{24}.12H_2O$
$(NH_4)_3SmMo_7O_{24}.12H_2O$.

The compounds are all isomorphous and chemically similar. With the yttrium elements it is difficult to get pure crystalline products by the same method.

Derivatives of Oxyhydroquinone.—G. Bargellini.—The author has prepared 2-4-5-trimethoxypropiophenone by allowing propionyl chloride to act on the trimethyl ether of oxyhydroquinone in presence of aluminium chloride. The compound thus formed fuses at 106—108°. When it is dissolved in methyl alcohol and treated with an aqueous solution of semicarbazide chlorhydrate and potassium acetate, a semicarbazone of melting-point 166—167° is obtained. The author has also prepared an oxime of trimethoxypropiophenone.

Measurement of the Charge carried by Magnetic Rays.—T. Collodi.—Righi has shown that a longitudinal magnetic field always produces a great diminution in the charge carried by the negative particles. This depends in certain states of rarefaction on the increase of ionisation produced in the interior of the protecting case. This increase of ionisation, which is fairly strong for slight rarefaction, diminishes as the latter increases. If the pressure is such as to allow the magnetic rays to have a fairly long path the diminution of the charge carried by the cathode particles remains very considerable.

Measurement of Surface Tension.—R. Magini.—Already noticed.

THE CHEMICAL NEWS.

Vol. CIII., No. 2680.

WHO FIRST SUGGESTED THAT THE RADIO-ACTIVE ELEMENTS ARE ELEMENTS UNDERGOING DECOMPOSITION AT ORDINARY TEMPERATURES?

By GEOFFREY MARTIN, B.Sc., M.Sc., Ph.D.

My attention has been called to the following passage, which occurs in the preface of Mr. Soddy's interesting book, entitled "The Interpretation of Radium" (1909):—"The present day interpretation of radium, that it is an element undergoing spontaneous disintegration, was put forward in a series of joint scientific communications to the *Philosophical Magazine* of 1902 and 1903 by Prof. Rutherford . . . and myself."

May I be allowed to point out that Messrs. Rutherford and Soddy were not the first to suggest that the radio-active elements are dissociating elements. So far as I am aware, the first definite statement to that effect occurs in the Chemical News of May 2nd, 1902, in a paper by myself entitled "The Radio-active Elements considered as Examples of Elements undergoing Decomposition at Ordinary Temperatures, together with a Discussion of their Relationship to other Elements." This paper was written on March 26th, 1902, at *Berlin University*, where I was engaged on a research on the alleged radio-activity of H_2O_2 vapours.

In my paper the following very definite statement occurs:—"For many years there has been a general disposition to revive the ancient notion that all matter is composed of a common 'protyle,' and that the elements have been formed from it by a successive series of condensations. And undoubtedly powerful experimental evidences has been furnished by the spectroscopic researches of Sir Norman Lockyer, who believes that the terrestrial elements are more or less completely dissociated into substances of a simple constitution at the high temperatures prevailing in the sun and stars. But what has hitherto been wanting is some experimental evidence that the elements do actually dissociate at temperatures attainable in the laboratory. But it appears that we now have this evidence, for the radio-active elements appear to be actually decomposing at ordinary temperatures." It is also definitely stated that "radio-activity" is a general property of matter—a conclusion now generally accepted. The paper attracted attention in America, and Prof. Baskerville, in his Presidential Address to the Chemical Section of the American Association (see *Nature*, Feb. 25, 1904, p. 403), did me the honour of referring to my work as follows:—"Many have theorised as to the ultimate composition of matter. The logic of Larmor's theory (*Phil. Mag.*, December, 1897, p. 506), involving the idea of an ionic substratum of matter, the support of J. J. Thomson's experiments (*Phil. Mag.*, October, 1897, p. 312), the confirmation of Zeemann's phenomenon, the emanations of Rutherford, Martin's explanations (Chemical News, 1902, lxxxv., 205), cannot fail to cause credence in the correctness of Crookes's idea of a fourth state of matter." Messrs. Rutherford and Soddy, therefore, cannot be credited with being *the first to put forward the theory that the radio-active elements are slowly decomposing*. All that they have done is to confirm by their brilliant experimental work my main thesis as regards the nature of the radio-active elements. Their first paper, "The Radio-activity of Thorium Compounds" (*Journ. Chem. Soc.*, 1902, lxxxi., 321), contains no statement of this theory. Their second paper (*loc. cit.*, p. 837) contains on p. 859 a statement of the theory in cautious language; this paper, however, was only published in June, 1902, *after the appearance of my paper*. Messrs Rutherford and Soddy's first communication to the *Philosophical Magazine* "On the Cause and Nature of Radio-activity" was published only in September, 1902.

THE PRECIPITATION OF ALUMINIUM HYDROXIDE IN THE GRANULAR FORM.

BY W. E. TAYLOR.

This device is put forward hoping that it will be a hint for those who continually have this estimation to make.

The chemist knows that by the ordinary method of precipitating aluminium trouble arises owing to the gelatinous nature of the precipitate, causing delay in filtering and washing; hours sometimes being required for these operations, tempting the chemist to wash the precipitate less times than he otherwise would. Several methods have been devised in order to get this worrying precipitate in a form to filter easily. A method enabling this to be done has recently been made known which consists of the use of a mixture of potassium iodide and potassium iodate, which answers fairly well, but the following may be found much more simple.

To the solution containing the aluminium, instead of boiling as in the ordinary way before adding the ammonium hydrate for precipitation, insert a thermometer, and precipitate at a temperature of 66° C., subsequently boiling as usual.

By doing this it will be found that, instead of having a gelatinous precipitate, it will have been precipitated in a granular form, which filters rapidly and freely.

As a result of a number of estimations it has been found that 66° C. is by far the best temperature to precipitate at, and that the results obtained checked with those obtained by the orthodox method.

63, King Street, Dudley.

ON NICKEL STEEL CASTINGS.

By SERGIUS KERN, M.E., St. Petersburg.

We introduce a certain quantity of nickel to our crucible steel in order to obtain perfect soundness in steel castings, subjected before delivery to serious trials; for instance, various steam-valves must stand hydraulic testing up to 600 pounds per square inch.

The crucible steel at the foundry of New Admiralty is prepared in coke furnaces. The charge per crucible is 100 pounds, and consists of 10·53 per cent of puddled iron (0·07 per cent of carbon, manganese—traces), 43 per cent of punchings from the rivet holes in soft shipbuilding plates, 44 per cent of rivet steel in ends and chippings, 1 per cent of nickel, and 0·15 per cent of 80 per cent ferro-manganese.

The furnace is fired at 11 a.m., and at 4 p.m. the castings are poured. The additions to the melted steel before pulling the crucibles out consist of:—

Ferrosilicon	0·60 per cent
Silicospiegel	0·65 „

Before pouring each crucible receives 0·07 per cent of aluminium.

The ferrosilicon contains 10 per cent of silicon, and the silicospiegel 10 per cent of silicon and 18 per cent manganese.

The resulting steel contains:—

Carbon	0·43 per cent
Nickel	0·72 „
Manganese	0·60 „
Silicon	0·37 „

After annealing, the steel mechanically tested gives about 50 tons per square inch of absolute resistance, and 10—12 per cent elongation in 2 inches.

It is interesting to note the loss in nickel in melting crucible steel.

THE WEIGHT OF A "NORMAL" LITRE OF HYDROGEN CHLORIDE AND THE ATOMIC WEIGHT OF CHLORINE.*

BY FRANK PLAYFAIR BURT and R. W. WHYTLAW GRAY.

(Concluded from p. 164.)

THE foregoing discussion leads to the conclusion that the chief errors in the determination of this constant are all of the same sign. The use of rubber vaseline grease, solution of gas in the lubricant, as well as adsorption, make the apparent density too large. In our measurements some of these errors were eliminated or minimised, and though our value, 1·63915 ± 0·00005 grms. per litre, is possibly still a little too high, we believe it to be accurate within small limits.

With the idea of putting these conclusions to an experimental test, we have devised a method of measuring the density of the gas, which eliminates error due to adsorption effects, and partially counteracts the influence of solution of gas in the tap grease. The gas was weighed, condensed on charcoal, as in our previous experiments, but instead of exposing the glass surface of the volume bulb to a vacuum, the gas was displaced from the latter by means of pure mercury, as in the adsorption experiment. The method adopted will be clear from the accompanying diagram (Fig. 3). The pressure of gas in the bulb, which was cooled to 0° C., was measured on a direct-reading manometer, and was adjusted closely to the neighbourhood of 760 mm. After the connecting tubes had been exhausted in the usual way by means of the subsidiary charcoal bulb C, mercury was allowed to enter the volume bulb at the same rate as the gas was absorbed in the weighing bulb B. The flow of gas could be regulated by gradually cooling B. During the process the mercury reservoir D was slowly raised so as to keep the internal pressure constant and approximately atmospheric. At the end of the operation mercury was allowed to pass through the tap bore a short distance into the capillary beyond, where it was frozen by means of solid CO_2 contained in a paper cup, not shown in the diagram. This cup was filled with CO_2 before the transference of the gas began, and served not only to freeze the end of the mercury thread, but also to condense any mercury vapour carried over by the gas in its passage, as well as to prevent the evolution of gas dissolved in the tap grease. Finally the bulb B was immersed in liquid air for a few minutes in order to absorb the gas remaining in the connecting tubes.

Any traces of mercury that escaped condensation by the CO_2 were absorbed in a tube E, which was tightly packed with fine gold wire.

At the end of the experiment dry air was let into the connecting tubes by breaking the point of the sealed capillary G.

The gas was prepared by the interacting of pure NH_4Cl and syrupy phosphoric acid in a vacuum, which previous experience has shown to give the purest product. In these experiments we have entirely dispensed with the use of P_2O_5 as a desiccating agent, and have used instead re-distilled anhydrous $AlCl_3$. The gas was first passed through a long tube containing mercury, and then dried, liquefied, fractionated, and finally sublimed, during which process the last traces of air were pumped off.

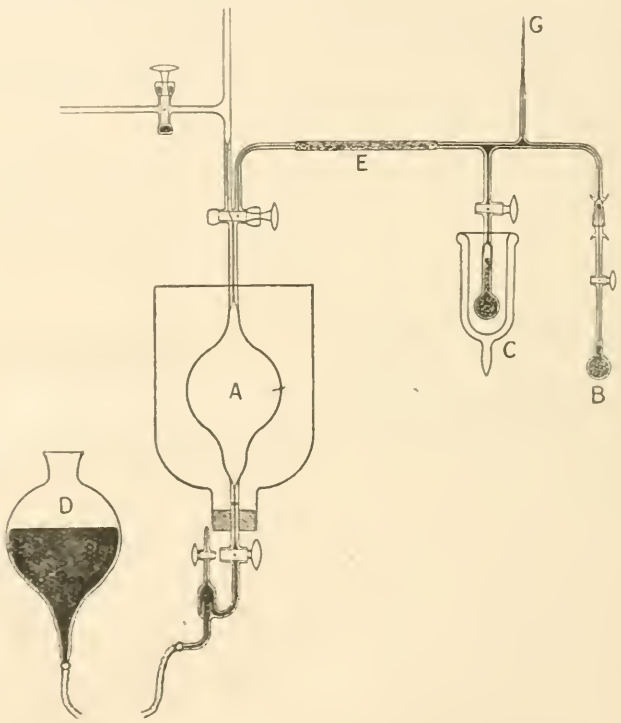


FIG. 3.

Scrupulous care was taken to ensure the thorough desiccation of the volume bulb. It was washed out for a long time with a stream of dry air, evacuated, and finally treated many times with pure dry HCl before making a determination.

We are unable to agree with Scheuer that hydrogen chloride must not be allowed to come in contact with mercury. We have never detected any reaction when the two substances were pure. Experiments carried out by one of us on the vapour pressures of this gas show that unless

* A Paper read before the Faraday Society, March 14, 1911.

both gas and metal are in a high state of purity a reaction does occur, which liberates hydrogen and forms mercurous chloride. On the other hand, when pure materials were employed no reaction was observed even at a temperature of 50° and under a pressure of 80 atmospheres. The compressed gas was allowed to stand in the experimental tube of a modified Andrews apparatus for several weeks, and at the end of this time no rise of pressure during liquefaction could be detected. Further, in our adsorption experiments the gas in the cylinders remained for months in contact with mercury, without impairing the lustre of its surface in the slightest degree, and without causing any stain at the junction of the metal and the glass. We have, however, repeatedly noticed that if the gas contains traces of air, chlorine and water vapour are formed on standing, and an appreciable film of chloride appears on any mercury surface exposed to the gas. In order to remove traces of chlorine formed in this way, the mercury tube already mentioned was used in the purifying train. The mercury for these experiments was purified by a prolonged agitation with aqueous hydrochloric acid, following the usual treatment with acid mercurous nitrate, and was afterwards dried by heating to about 200° C.

Finally, the following experiment demonstrated conclusively that no action between the mercury and the gas took place under the conditions of these experiments: The volume bulb, half-filled with mercury, was allowed to stand in contact with the pure gas for 65 hours (the usual exposure during a determination rarely exceeded half-an-hour). At the end of this time the gas was passed into a few cc. of strong aqueous potassium hydroxide, which had previously been boiled. The 275 cc. of gas were completely absorbed, with the exception of a minute bubble of a volume not exceeding 2 cub. mm. No appreciable additional quantity of gas was obtained on boiling the solution *in situ*. The volume of the unabsorbed gas was less than 1/100,000 part of the whole, and could not have affected the results.

Calibration of the Volume Bulb.

The bulb was calibrated by determintng the weight of mercury, which at 0° C. exactly filled it from a mark on the lower capillary up to but not including the tap bore. Two separate determinations gave for the weight of mercury—

(1) 7495·316 grms.
(2) 7495·282 grms.

corresponding to the volumes—

(1) 551·309 cc.
(2) 551·306 cc.

Mean .. .. 551·308 cc.
Vac. arr. for air displaced by mercury .. +0·050 cc.

True volume .. 551·358 cc.

The weights used were re-calibrated for this series of experiments, and their relative values determined by weighing the pieces against each other in air. No corrections were made for the air displaced by the weights themselves, for reasons already given (*Trans. Chem. Soc., loc. cit.*). The height of the manometric column was expressed in terms of a different scale to that used in the previous density determinations, the one subsequently employed in our compressibility measurements. These precautions were taken with the object of detecting any constant errors which might have crept into our previous work. The results themselves are contained in Table IV.

The agreement of the individual results is distinctly better than that previously obtained, the maximum divergence being 4·4 in 10,000. The weight of a normal litre is hence $\frac{1{\cdot}64011}{1{\cdot}000588} = 1{\cdot}63915$ grms. (where 1·000588 is the factor which expresses difference in the value of "*g*" between London and lat. 45°), and is identical to the fifth place of decimals with our previous result.

Table IV.

No.	Pressure.	Weight.	Weight of a litre of gas at 0° and 760 mm., lat. London.
1.	755·20	0·89835	1·63977
2.	753·68	0·89665	1·63999
3.	755·89	0·89934	1·64007
4.	744·11	0·89716	1·63999
5.	754·72	0·89816	1·64049
6.	756·08	0·89943	1·63982
7.	756·63	0·90024	1·64009
8.	755·98	0·89949	1·64016
9.	756·12	0·89978	1·64037
10.	756·73	0·90047	1·64030

Mean .. 1·64011 ± 0·00005

Such a close agreement is no doubt accidental, since it is less than the probable experimental error, but nevertheless it affords a strong confirmation of the correctness of our former work.

The whole of our results on the density of this gas may be summarised as follows:—

Series.	Source of gas.	Number of experiments.	Volume of bulb.	Mean weight of a normal litre. Grms.
I.	$NaCl$ and H_2SO_4	4	465·856	1·63907
II.	$SiCl_4$ and H_2O	7	465·856	1·63914
III.	NH_4Cl and H_2SO_4	10	457·420	1·63920
IV.	NH_4Cl and H_3PO_4	10	551·358	1·63915

The gas was prepared from four different sources. In Series I., II., and III. it was dried by phosphoric anhydride, in Series IV. by anhydrous aluminium chloride. The gas was fractionated many times and in a variety of ways, and it was also sublimed at low pressure without any detectable alteration of density. The gas itself was absorbed completely by solid caustic potash, and the unabsorbed residue remaining after treatment with boiled aqueous caustic potash was negligibly small. The density bulb in Series I., II., and IV. was of glass, in Series III. a fused silica one was used. In all cases the gas was weighed condensed on charcoal in a bulb of small volume, but in Series IV. the method was varied by displacing the gas from the density bulb at constant pressure by means of mercury, and by using a different set of weights and a different manometer scale. In all thirty-one determinations were made, and the arithmetic mean gives the value—

1·63915 ± 0·00004 grms.

as the weight of a normal litre of hydrogen chloride.

This result does not modify our previous conclusions, and we wish to express our belief that the most probable value for the atomic weight of chlorine yielded by physico-chemical evidence is 35·460, a value which is identical with that adopted by the International Committee for Atomic Weights in their report for 1910.

City and Guilds of London Institute.—The Council of the City and Guilds of London Institute have elected E. Frankland Armstrong, Ph.D., D.Sc., F.C.S., a Fellow of the Institute (F.C.G.I.) in recognition of his original and valuable research work and his contribution to the advancement of the industry in which he has been engaged since he gained the Associateship of the Institute at the close of his regular course at the City and Guilds Central Technical College in 1903. In addition to his contributions to chemical science Dr. Armstrong has been actively concerned in the introduction of a new protein biscuit by Messrs. Huntley and Palmer of unique food value in a concentrated form, which has been selected as the main article of food to be used during Captain Scott's sledging expedition to the South Pole.

THE FRUIT OF THE *CORNUS PANICULATUM.*

By GUINNEVERE SHEETS.

THE fruit of the *Cornus paniculatum* was gathered on the Campus of Cornell College, Mount Vernon, Iowa, and other places in the vicinity, during September, 1907-8. The fruit was found on small trees in panicled clusters.

The fruits, which are drupes, have a decidedly sweet taste, and when dried are brownish black in colour and resemble commercial currants. When burned the odour resembles burnt wood at first, and afterwards coffee. There is a large hard seed or stone in the fruit which renders difficult the crushing with mortar and pestle. The average weight of each when dried was 0·0762 grm.

The Sugars.

About 100 grms. of the dried fruit were taken for the sugar extraction. These were placed in a 500 cc. flask fitted with an inverted condenser, and treated with successive portions of 95 per cent alcohol for about thirty days. The extract was removed each day, and a fresh portion of alcohol added. The alcohol was distilled off, and a thick syrup remained behind. The odour of the first extraction bore a strong resemblance to new cider. In a short time the odour resembled old cider, and a test for acetic acid showed that fermentation was taking place.

At the end of thirty days a test with Fehling's solution showed that the sugars were nearly extracted, and distilled water was substituted for the alcohol.

The fruits remained hard and firm under the alcoholic treatment, while on the addition of water they became soft and mushy. The alcoholic extract at the end of thirty days was nearly colourless, while at first the water extraction was nearly black. Ten days were required to remove all coloration and the remainder of the sugars by the water treatment.

The amount of the sugars was determined by Fehling's solution of such strength that 10 cc. corresponded to 0·05 grm. of sugar. The determination was made by taking 1 cc. of the sugar extraction and diluting with 50 cc. of water in a small beaker. This was heated to boiling and titrated with Fehling's solution. To determine when the end-point was reached a small portion of the solution was filtered from time to time, always pouring the filtrate back until the sugars had no more reducing power. The filtrate became of a greenish colour, and when reduction was complete it assumed a light blue tint. The blue colour could be produced by three drops of Fehling's solution when the end-point was reached, and so it seemed a satisfactory test. There was found to be 78·98 per cent of sugar in the dried fruit.

A portion of the filtrate containing the sugars was digested for twenty-four hours on the warm water-bath with a relatively large amount of purified bone-black. The bone-black was removed by filtration, and a portion of the filtrate was evaporated on the water-bath to constant volume, a thick brownish coloured syrup remaining. We weighed out 0·2 grm. of this residue, and treated it with phenylhydrazine and sodium acetate according to Sherman and Willlams (*Journ. Am. Chem. Soc.*, xxviii., 629). The time of the osazone formation was two minutes, which indicates fructose. We repeated the experiment several times, and always with the same result. The test with cobalt nitrate gave some indication of dextrose, so it is quite likely both are present.

As a larger quantity of residue was needed for oil extraction it seemed likely that the sugars might be removed more rapidly by using a litre flask and larger quantities of the solvent and changing twice daily. In two weeks all the sugar was extracted.

The Acids.

The acid tests were made from the sugar extractions. Tartaric, citric, and acetic acids were found. The last, however, doubtless resulted from fermentation.

The Ash.

Five portions of the fruit of exactly 2 grms. each were ashed in a platinum evaporating dish. From the first, silica, iron, alumina, calcium, and magnesia were determined; from the second portion the sodium and potassium were removed by the J. Lawrence Smith method; from the third portion, the sulphates; from the fourth, the phosphates; and lastly, manganese and chromium were looked for, but not found. The results of the analysis are as follows:—

	Per cent of the ash.
K_2O	14·51
Na_2O	14·78
Al_2O_3	1·88
Fe_2O_3	1·88
CaO	14·63
MgO	22·88
Mn	0·0
Cr	0·0
P_2O_5	21·35
SO_3	3·61
CO_2	1·41
	96·93

Five other portions were treated in the same way, and the results agreed very closely with the first.

The Proteins.

Some of the fruits were crushed and boiled in distilled water for a short time. A small amount of this solution was heated with nitric acid, giving a yellow colour which changed to orange-red when made alkaline. This shows the presence of albumen.

The nitrogen was determined by the Kjeldahl method, 2 grms. of the fruits showing a nitrogen content of 0·56 per cent.

The Oils.

The 165 grms. of fruit from which the sugars had been removed were dried and ground in a small coffee mill. The powder was placed in a 590 cc. flask, which was tightly fitted with an inverted condenser, and treated with ether. Two weeks were used in extracting the oil, which after removing the ether by distillation was of a clear amber colour. To purify it we heated the oil for thirty hours with ether and bone-black, again using the inverted condenser, and then filtered.

There were two distinct kinds of oil, one amber-coloured, which seemed to be palm oil, and the other a pure white. The specific gravity of a mixture of the two was 0·8733, which is approximately the specific gravity of cocoanut oil. The oils easily solidified in a freezing mixture, but quickly melted upon removal from the same.

The white oil became thick upon exposure to the air, and the sides of the flask in which it was contained resembled frosted glass. The total amount of oil obtained after drying in an oven at 95°—110° was 19·23 grms., or 11·6 per cent of the dried fruit.

The oils were saponified by Koetstorfer's process. 1·1996 grms. in a flask were connected with an inverted condenser. We added 25 cc. of normal caustic soda solution and the same quantity of alcohol. This was kept on a boiling water-bath for nearly eight hours, when a complete solution of the oil took place. Phenolphthalein solution was added, and the alkaline solution was titrated with normal hydrochloric acid. The saponification equivalent was thus found to be 218, which indicates cocoanut oil. The products of the saponification were separated. The soapy solution was diluted with distilled water, and a quantity of ether was added, which dissolved the unsaponifiable portion. This was separated from the liquid and evaporated to constant weight. This residue was dissolved in hot alcohol and filtered, and left to evaporate spontaneously. Some fine white crystals separated out.

After separating the ethereal layer the remaining liquid was acidified with sulphuric acid and slightly warmed, whereupon the fatty acids liberated by saponification collected upon the top of the liquid. These were separated from the water, dried on the water-bath, and found to weigh 0·2157 grm. The characteristics of this pointed to cocoanut oil. It reacts acid to litmus-paper.

The ashes of the portion of the solid fruit that remained after the oil extraction were analysed. The results did not differ greatly from what was obtained from the original fruit, but about three times the weight of material was required to furnish the same amount of ash.

I wish to express my thanks to Dr. N. Knight for advice and assistance in this week.

Cornell College, February 24, 1911.

IONISATION OF GASES AND CHEMICAL CHANGE.*

By H. BRERETON BAKER, M.A., D.Sc., F.R.S.

The term "catalytic" was introduced by Berzelius to describe a number of chemical actions which would only take place in the presence of a third substance, which itself was apparently unchanged throughout the reaction. The first cases of such actions were investigated by Sir Humphry Davy in 1817. He showed that many mixtures of gases were caused to unite in the presence of finely divided platinum, at temperatures far below those at which union ordinarily took place. Some years afterwards Faraday investigated similar actions, and attempted to explain them by a supposed condensation of the gases on the surface of the metal.

Thirty years ago, Prof. H. B. Dixon investigated the behaviour of carbon monoxide and oxygen when they were dried as completely as possible, and he discovered that under these circumstances electric sparks caused no explosion. Some years before, Wanklyn had discovered that purified chlorine did not act on sodium, but he did not identify the impurity, now known to be a trace of water, which causes the vigorous action which takes place under ordinary circumstances.

In 1882 Cowper investigated the action of dried chlorine on several metals, and found that the removal of moisture in many cases inhibited the reaction.

In the following year, working in Prof. Dixon's laboratory at Balliol College, I found that purified carbon could be heated to redness in dried oxygen, and that sulphur and phosphorus could be distilled in the same gas without burning. In the investigations which followed, some thirty simple reactions have been tried by myself and others. It has been shown that hydrogen and chlorine can be exposed to light without explosion, ammonia and hydrogen chloride mixed without union, sulphur trioxide can be crystallised on lime, ammonium chloride and mercurous chloride give undissociated vapours, hydrogen and oxygen can be exposed to a red heat without explosion, and lastly in 1907 nitrogen trioxide was obtained as an undissociated gas for the first time by carefully drying the liquid and evaporating into a dried atmosphere.

The amount of water necessary to carry on these chemical reactions is extremely small, certainly less than 1 mgrm. in 300,000 litres. There is no accepted explanation of its catalytic effect, and in the same way the catalytic power of platinum is still a mystery. In 1893, Sir J. J. Thomson (*Phil. Mag.*, xxxvi., 321) showed that if the combination of atoms in a molecule is electrical in its nature, the presence of liquid drops of water, or drops of any liquid of high specific inductive capacity, would be sufficient to cause a loosening of the tie between the atoms, and this might result in chemical combination of the partially freed atoms to form new molecules. He showed in the same paper that drying a gas very completely stopped the passage of a current of 1200 volts. In the same year I was able in the same way to prevent the passage of discharge from an induction coil, a discharge which would traverse a spark gap of three times the distance in undried gas.

Shortly after the discovery of Röntgen rays it was found that they would ionise a gas through which they passed. At the time it was thought that this ionisation was similar to that taking place in electrolysis. If this were so the rays would probably cause chemical union to take place even in a dried gas, and accordingly Prof. Dixon and I undertook some experiments on the subject which were published in a joint paper (*Chem. Soc. Journ.*, 1896). The results were negative, no chemical action could be detected. Since that time the ionisation of gases has been shown to be of quite a different nature. The negative ion has been shown to be a particle of the mass of about 1/1500th that of the hydrogen atom, and the positive ion is the residue. Since the ionisation of gases is different from that in electrolysis, the retention of this term is much to be deprecated. It is suggested that the term ionisation should be retained for electrolytic dissociation, and for the different process which takes place in gases under the action of Röntgen rays, &c., a new name, electromerism, should be adopted. The electron would thus be the negative electromer.

It is probable that electrolysis and true ionisation may take place in gases, as in the decomposition of steam by electric sparks of a particular length. An experiment, recently devised, seems to show that in mercury vapour, which ordinarily consists of atoms, something of the nature of ionisation without electrolysis can take place. If oxygen be admitted to the interior of a mercury lamp from which the current has just been cut off, a considerable quantity of mercuric oxide is produced, although the temperature of the lamp (about 150°) is far lower than would suffice to bring about the union of ordinary mercury vapour with oxygen.

In order to test further the question as to whether electromerism can bring about chemical change, I have investigated the action of radium bromide on very pure and dry hydrogen and oxygen. The gases were sealed up with some radium bromide contained in an open silica tube. The containing vessel was provided with a vacuum gauge, by means of which the combination of 1/5000 part of the gases could be easily detected. No action whatever was observed, although the substances were left in contact for two months. A further experiment showed that, as was to be expected, very dry air undergoes electromerism when subjected to the action of radium. Two more tubes were then set up, similar to the first, containing mixtures of carbon monoxide and oxygen, one very dry, and the other containing traces of moisture, and although the radium bromide was in contact with them for more than three months not the slightest contraction could be observed. In these cases therefore electromerism produces no chemical change.

There, was, however, a possibility that electromerism might bring about a chemical action in a mixture of gases which was under conditions which were nearly, but not quite, suitable for chemical action to take place. The gaseous mixtures mentioned only combine, even when moist, at a red heat. Since the experiments were done at 20°, they only show that electromerism does not produce chemical action in gases which are otherwise unable to combine.

There remained the possibility that if gases were just on the point of combining, increasing the electromerism might accelerate the rate of action. I sought for a case of simple chemical union which would proceed at a manageable temperature, and at a rate which could be measured. Of those tried, the reaction between hydrogen and nitrous oxide was found to be the most suitable. The gases used were as pure as possible, but dried only by passing through phosphorus pentoxide tubes. They were found to combine

* A Discourse delivered before the Royal Institution, March 11, 1910.

with great uniformity when heated in clean Jena glass tubes to 530°. An electric resistance furnace was used, consisting of a wide silica tube which formed the heated chamber. It is known that many substances when heated produce electromers in a gas; lime is fairly efficient, thoria more so, and of course, radium bromide most of all. In the first experiment two tubes of the same Jena glass, containing the hydrogen and nitrous oxide mixture, were heated side by side. One contained some lime, and in order to make the conditions as similar as possible, an equal quantity of powdered Jena glass was introduced into the other. As soon as the requisite temperature was reached, the action proceeded rapidly in the tube containing lime, the rate in the first five minutes being five times the rate of combination in the tube containing only powdered glass. After fifteen minutes the second tube had caught up the first, and the rates of union were equal up to the completion of the action. With thoria the effect was still more marked, the rate increasing to twenty times the rate in the tube containing the glass. Finally about 2 mgrms. of radium bromide was heated in the mixture of gases. As soon as the combining temperature was reached the gases in the radium bromide tube exploded.

From these three experiments it is seen that as the amount of electromerism was increased, there was a rapid increase in chemical action.

I have recently been able to show that if the union of carbon monoxide and oxygen takes place in a strong electric field, which has the effect of removing electromers, the chemical action is diminished. Similar experiments are in progress with the mixture of hydrogen and chlorine, combining under the influence of light.

The next experiment tried illustrated one way in which the electromerism of a gas may bring about chemical change. Hydrogen sulphide and sulphur dioxide can be mixed at the ordinary temperature in presence of traces of moisture, but in presence of liquid water, decomposition takes place into sulphur and water. The gases were dried before mixing by calcium chloride, which leaves about 4 mgrms. of water vapour per litre in the gas. After mixing, a small open silica tube containing about 2 mgrms. of dried radium bromide was introduced. After six hours no apparent change had taken place in the gas; there was no deposit of sulphur on the sides of the jar, and it seemed at first as if no action had been produced. On opening the jar, however, an inrush of air was noticed, and the contents were almost odourless. On heating the radium tube a large quantity of water was driven off, and a copious sublimate of sulphur was seen. The whole of the gaseous contents of the jar had condensed in the small tube containing the radium bromide. The explanation of this action of radium bromide is probably simple. Water vapour condenses on the electromers emitted, liquid drops are formed, and in them the chemical action takes place.

(Note.—I have invariably notice that water collects in tubes containing radium preparations exposed to undried air. The salts are not at all deliquescent, the crystals appearing quite sharp-edged under the miscroscope. I found that 10 mgrms. of radium bromide exposed to an atmosphere saturated at 0° for two days caused a deposition of water on its surface weighing 1·5 mgrms.).

Prof. Townsend has recently published an account of some experiments, in which he has shown that there is a very marked decrease in the mobility of negative electromers in the presence of an amount of water vapour represented by a pressure of one-tenth mm. The air, in his experiments, was subjected to the action of Röntgen rays.

It is concluded that water in a form approaching to that of a drop, is condensed on the electron even when a very small quantity is present. If this deposition of water molecules on electromers goes on when the amount of water present is still smaller, the theory of Sir J. J. Thomson affords a satisfactory explanation of the influence of moisture on chemical change, since some electromers are always present in ordinary gases.

THE ELECTROLYTIC DETERMINATION OF ZINC IN ORES.

By GEO. KEMMERER.

The investigation was undertaken to ascertain if the zinc content of an ore could not be accurately and quickly determined electrolytically.

The original plan was to separate the zinc from the other constituents of the ore, as zinc sulphide, by a method similar to the "Modified Waring"; this sulphide was then to be dissolved in a little acid, the hydrogen sulphide boiled out, made alkaline with sodium hydroxide, and electrolysed.

Numerous experiments with an ore of known zinc content, using an electrolyte containing from 7 to 10 grms. of sodium hydroxide, give high non-concordant results.

About this time E. B. Spear, E. E. Wells, and B. Dyer (*Journ. Am. Chem. Soc.*, xxxii., 530) showed that several methods gave high results, and Spear (*Ibid.*, xxxii., 533) stated that the high results were due to zinc oxide, or hydroxide deposited with the zinc, and suggests that a strong alkaline electrolyte might prevent this, but proved that it is theoretically impossible to deposit all the zinc from such an electrolyte. Harrison Hale ("Thesis U. of P.," 1908) determined the zinc content of a pure blend, using an electrolyte containing 15 grms. of sodium hydroxide. His results were not high, and the average of a large number of determinations was very close to the gravimetric results.

Experimental.—The electrolytic cell used consisted of a cylindrical nickel gauge cathode which fitted loosely into a 150 cc. Jena beaker, and a revolving propeller-shaped anode.

The cathode surface was about 160 sq. cm., while the anode was rotated about 600 times per minute.

Weighed pieces of C. P. zinc were dissolved with nitric acid in a 180 cc. flask, 2 cc. of sulphuric acid added, and evaporated to dense fumes of sulphur trioxide. After cooling, the contents of the flask were rinsed into a 150 cc. beaker, diluted to 100 cc., and stick sodium or potassium hydroxide added. This heated the solution nearly to boiling, and it was electrolysed at once.

When the deposition was complete the cathode was removed without opening the switch, and plunged into a large beaker of water. It was then dried with absolute alcohol, and ether, which had been distilled over sodium, heated to 70—100°, cooled, and weighed at once.

The gauze electrodes cool quickly, and it is important to weigh at once, for on standing the deposits gain in weight.

	Weight of deposit.		Weight after standing in desiccator.	Gain.
1 ..	0·2501	Over night ..	0·2505	0·0004
2 ..	0·2500	Two hours ..	0·2504	0·0004
3 ..	0·2517	One hour ..	0·2521	0·0004

After the electrolysis the solution remaining was always tested for zinc by acidifying with dilute sulphuric acid, cooling to 60° and adding 50 cc. of 10 per cent solution of potassium ferrocyanide. This test, as shown by E. B. Spear, E. E. Wells, and B. Dyer (*Journ. Am. Chem. Soc.*, xxxii., 530), was found to produce a turbidity with 0·5 mgrm. of zinc in 200 cc. of solution.

After weighing the deposits, the zinc was dissolved from the nickel cathode in 2 to 3 per cent sulphuric acid. By this treatment the cathode loss was kept below 0·5 mgrm., but it gradually darkened, due to a trace of lead in the zinc. After ten to twenty determinations the black deposit was removed by pouring a little nitric acid over the electrode.

With an electrolyte containing from 7 to 10 grms. of sodium hydroxide the results ran as much as 0·9 per cent high, and were not concordant.

When the alkali was increased to 20 to 25 grms. the following results were obtained:—

	A.	V.	Time.	Zinc taken.	Zinc found.	Error.
1 ..	6	4·4	15	0·1762	0·1759	−0·0003
2 ..	6	4·2	15	0·2099	0·2019	—
3 ..	5	3·8	15	0·3180	0·3184	+0·0004
4 ..	5·2	3·8	15	0·3740	0·3743	+0·0003
5 ..	5	4·0	15	0·2412	0 2410	−0·0002
6 ..	5	4·0	10	0·2502	0·2501	−0·0001
7 ..	5	4·2	14	0·2502	0·2500	−0·0002
8 ..	5	4·2	15	0·2502	0·2496	−0·0006
9 ..	6	4·4	20	0·2149	0·2147	−0·0002
10 ..	6	4·4	20	0·2149	0·2144	−0·0005

The deposits were all a beautiful bluish white, and in every case the remaining solution showed no zinc present by the ferrocyanide test.

These results seem to justify the application of the method to ore analysis, so a simple carbonate ore was chosen, the zinc content of which had been determined several times before this work was started. It contained 42·35 per cent zinc, 9 per cent iron, no lead. It was treated by the modified Waring method given in Low's "Technical Methods of Ore Analysis" as follows:—

"After decomposing the weighed sample by acids alone, or aided by fusion, as the case may require, all the zinc is to be brought into solution as sulphate. If nitric acid was used in the decomposition, all traces of it must be expelled by evaporation with hydrochloric and sulphuric acids successively, or by two evaporations with sulphuric acid, finally to abundant evolution of SO_3 fumes. Dissolve the mass in 25 to 40 cc. of water, and add sufficient sulphuric acid to bring the free acid in the solution up to 10 or 15 per cent. Introduce a piece of heavy sheet aluminium, and boil ten minutes or to complete reduction. Filter and wash through a filter containing a piece of aluminium into a beaker containing a stirring-rod or strip of the same metal, cool, add a drop of methyl-orange, and neutralise carefully with *sodium bicarbonate* to a light straw colour. Add, dropwise, dilute formic acid (20 per cent strength) until the pink colour is just restored, then 5 drops more. (Dilute hydrochloric acid, 1 part strong acid to 5 parts water, may be substituted for formic acid when ammonium thiocyanate is to be introduced). Dilute to about 100 cc. for each 0·1 grm. of zinc possibly present, add, if much iron is present, 2 to 4 grms. ammonium thiocyanate, remove the strip of aluminium, heat nearly to boiling, and saturate with hydrogen sulphide. Allow the pure white zinc sulphide to subside for a few minutes, then filter and wash with hot water."

The zinc sulphide was carefully washed with hot water, and dissolved on the filter in a little hot dilute hydrochloric acid. To this solution in the 400 cc. beaker in which the sulphide was originally precipitated 2 cc. of sulphuric acid were added, and the whole allowed to evaporate until most of the sulphuric acid was driven off. The zinc sulphate was then rinsed into a 150 cc. beaker, diluted to 100 cc., 25 grms. of sodium hydroxide added, and electrolysed.

The nickel gauze cathode previously described was used, and a current of 6 ampères at a pressure of 4·4 volts was allowed to flow for fifteen minutes, while the anode revolved about 600 times per minute.

The results were concordant, but always about 0·3 per cent high.

Several of these deposits were dissolved, the iron determined colorimetrically, and found to be equal to 0·0014 to 0·0016 grm. of iron. When using a ½ grm. sample of ore this would equal 0·3 per cent.

The sodium hydrate was carefully tested, and did not contain more than a trace of iron, so that this large amount must have been carried down with the zinc sulphide.

After numerous experiments it was determined that if 4 to 5 drops of concentrated hydrochloric acid in place of 5 drops of 1—6 were added to the neutral solution before precipitating the zinc sulphide, that in the presence of ammonium sulphocyanide all the zinc was precipitated as sulphide free from iron.

With this modification the ore containing 42·35 per cent of zinc gave the following electrolytic results:—

Weight of ore.	A.	V.	Time, mins.	Zinc found.	Per cent.
0·5000	5	3	15	0·2116	42·32
0·5007	6	4·2	15	0·2114	42·22
0·4995	6	4·2	15	0·2107	42·18
			Average		42·24

The next ore was a standard sent out by the New Jersey Zinc Company. The results by various chemists ran as follows:—35·5, 35·57, 35·5, 35·2, 35·5, 35·67, 35·87, 35·7; average, 35·56.

Electrolytic Method.

Weight of ore.	A.	V.	Time. mins.	Zinc found.	Per cent.
0·5002	6	4·2	15	0·1792	35·83
0·5003	6	4·2	15	0·1783	35·64
0·5002	6	4·2	15	0·1794	35·86
0·5009	6	4·2	15	0·1790	35·73
0·5007	6	4·2	15	0·1790	35·77
			Average		35·77

Each of these deposits was tested for iron, and not more than a trace was found.

All the results obtained for this ore, including those corrected for iron, are as follows:—35·73, 35·74, 35·74, 35·57, 35·67, 35·83, 35·64, 35·86, 35·77; average, 35·73.

Conclusions.

This work has proven that zinc can be accurately determined electrolytically; that the results are not high if the electrolyte contains from 20 to 25 grms. of sodium hydroxide, and with a current of $N.D._{100} = 3·1$ A, all the zinc can be deposited; that this method, which is shorter than the usual gravimetric procedure, gives results fully as accurate. — *Journal of Industrial and Engineering Chemistry*, ii., No. 9.

LOWELL OBSERVATORY PHOTOGRAPHS OF THE PLANETS.*

By Prof. PERCIVAL LOWELL, A.B., LL.D.

THE pictures which I have the honour of showing you to-night represent the results of the new planetary photography originated at Flagstaff in 1903—1905, and now beginning to be successfully copied elsewhere, notably this last summer by M. le Comte de la Baume-Pluvinel and M. Baldet in France, who from the summit of the Pic du Midi de Bigorre succeeded themselves in getting imprints of the canals of Mars. Although the method was originally designed to exhibit the markings of what is practically our nearest neighbour in space, it has since been applied to the other planets with an outcome as surprising as it is satisfactory. Little details which one would not have supposed could set still long enough for their pictures to be taken stand out unmistakably on the plates; the faint equatorial wisps of Jupiter offering a good example of such tractability, though by no means the most remarkable.

That the canals of Mars should be made to write their own signatures on a photographic plate was the occasion of the invention of the process, which, after long and patient study by my assistant, Mr. Lampland, they were finally induced to do. To his marvellous feat the best tribute was that of Schiaparelli, who, after recognising the canals on the print sent him, wrote me in wonder that photography could be made to do such work, "I would never have believed it possible." Since then further improvement has been reached to which almost every member of the staff has contributed. The process is based upon what our visual study of the planets has taught us to be the crux in the matter: the all-importance of definition. For this reason the older celestial photography, which furnishes such

* A Discourse delivered before the Royal Institution, April 8, 1910.

beautiful pictures of the stars and nebulæ was here impotent. This will be realised when one considers that the whole disk of a planet could be put inside the image of a single star. For a like cause reflectors cannot be employed; for with them all faults, instrumental or atmospheric, are magnified three-fold over those of a lens. They may give imposing-looking pictures, but the finer detail is lost; a fact which is evident at once to an expert. Now it is in the registration of this finer detail that the accomplishment lies, and which from a scientific point of view marks its importance.

Study of the conditions leading to definition has made these photographs possible, just as lack of such study alone makes possible the scepticism one sometimes hears. Thus it is a well-known fact with us that the main markings of a disk may come out sharp, while the delicate ones are obliterated by a blur which otherwise eludes detection. This applies as much to photographic as to visual results, and it is this defect that a reflector introduces. Another optical mistake, which has latterly been hailed as showing that the lines are not lines but a series of dots, was made the other day in France. The observer saw perfectly correctly, but one with knowledge of the optics of a telescope in our air should have known that the effect observed was the inevitable result of using an aperture which the seeing did not warrant, as he could easily have assured himself by looking at the shattered rings in the synchronous image of a star. Even in our far better Flagstaff atmosphere the best results are got by diaphragming the aperture down.

In photography we cannot diaphragm down to advantage because we need the light, and this is one reason why photographs cannot rival an expert eye. Visual observations conducted by an eye fitted by nature, and trained by experience, must always surpass the best the camera can do.

What the new process does do is to monochromatise the light as nearly as possible. This is accomplished by a colour-screen, and a plate sensitised in accord with it. Then at the moment of exposure every precaution is taken that all movement shall be as nearly nil as can be secured within the instrument itself and in the air without it. Lastly, he who would photograph the canals most successfully must first have seen them, that he may know when his opportunity arrives.

Planetary photography is not intended, nor is it destined, to supersede visual observation. Research on the planets must rest in future, as in the past, on the ultimate power of the eye and of the brain behind it, whether this take the form of telescopic, spectroscopic, or other perhaps new line of inquiry. But in certain ways the sensitive plate may supplement the retina. Position is one of these, contrast another. For the eye to place in their proper posts all the markings of a multi-featured disk in the short time at its disposal is a well-nigh impossible task. The film registers them at once in situ. Values are another thing the photographs being out clearly. They exaggerate contrast, it is true, as compared with the eye; but this is no detriment. Rather the reverse, for it furnishes a greater scale for measurement.

In looking at the paragraphs two things must be borne in mind. One is that the irregularities due to the grain of the plate must not be attributed to the images. Thus, within the limits set by the grain the lines on Mars show as lines, not as a patchwork. This is perfectly apparent when they are carefully scanned. When we consider that the original images are only 5 mm. in diameter we realise the strain of lantern exhibition. Even so they are magnfied 200 times in the taking. They are then further enlarged on the slide, and lastly thrown greatly increased upon the screen. The wonder is that they stand this limelight publicity at all.

The second point is that we are not dependent on them for our minute knowledge of the planet. A good eye trained to the subject sees at least ten times as delicately as the film. But it must be an eye suited to planetary work, which is quite a different eye from that good at faint satellite or nebula detection. It is very important to remember this, for not only is there a physiologic reason for it, but mistake of it is often made in high quarters. When an observer records a polar flattening as twice and four times what hydrodynamics permit, his forte lies elsewhere than in planetary research.

Three planets will now show you their presentments: Mars, Jupiter, and Saturn. I was minded at first to omit Mars, passing by this old acquaintance with a nod, but so great have I found the interest in him here as elsewhere that he has been put beside the others.

As an example of the delicacy of the detail to be described on him, not only by the eye but in the photographs, may be instanced the sight of one of the many vicissitudes of his changeful year, which suddenly appeared one day when least expected. The event was the first frost of the season in the Antarctic regions of Mars, detected visually at Flagstaff on November 16. The patch was at once photographed, and is plainly apparent on the plate. To chronicle thus the very weather on our neighbour will convince anyone that interplanetary communication has already begun, and that, too, after the usual conventional manner of ordinary mundane greetings.

My next mention shall show you the pitch of precision to which measurements of these little prints can attain. It is well known that the south polar cap of Mars is not centred on the pole, but lies some 6° off it, in longitude 20° or thereabouts. When the images showing the cap at two different longitudes were measured the measures revealed distinctly the excentring of the cap, and even registered with some accuracy its amount and position. When we reflect what this means, it looks as if Mr. Crommelin's belief that areology would stand indebted to the photographs for help in its geodetic survey is in a fair way to be realised.

It would be possible in these photographs to take you on many a journey to that other world, but to-night one more such interplanetary voyage must suffice. This shall give you sight of the great new canals that appeared last September in a region of the planet where no canals had ever showed before. That you may fully realise what you are to see the plate shall be accompanied by a drawing in which of course the phenomenon stands much better displayed, and a word of preface may not be out of place. To begin with, you should know that the lines you will see are certainties, not matters admitting of the slightest question for all their strange regularity, and so seen by all those who from the most prolonged and careful study are qualified to speak. Schiaparelli described them as looking as if they had been laid down with rule and compass, and not only I, but all of my assistants, have seen them thousands of times the same. Nor are they near the limit of vision in our air, which sometimes sets the planet against the sky as if etched in a steel engraving.

In the second place, the technical word "canals" does not mean canals that are dug, but artificially fertilised strips of country, connected with, and vivified by, the turning to such account of the melting of the polar cap. Lastly, I may say that by saying that the organic life exists there we do not mean human beings. And now to the facts recently observed.

On September 30 last, when the region to the east of the Syrtis Major came round into view again after its periodic hiding of six weeks due to the unequal days of the Earth and Mars, two imposing canals were seen leading up from the Syrtis to the south-east, which had not been there at the preceding presentation. Research showed that not only had they never previously been seen, but that they could never have existed as such before. The long and full records of the observatory extending over fifteen years made it possible to be absolutely sure of this. Yet these canals with several subsidiary ones fitted into the general canal system as if they had always made part of it.

Not only was their coming into existence established by the drawings, but the photographs of previous years

testified to the same unheralded advent. Their presentments on the screen will show you this, and by comparing the drawings and photographs made at the same epoch the oneness of the two becomes evident, while the change of both with the Martian seasons is clearly portrayed.

Turning now to Jupiter, we find a completely different set of features registered on the plates, no less corroborative of the drawings made of him at Flagstaff, but utterly unlike those of Mars. Their symmetry is immediately striking, and then no less is its purely latitudinal character. They are belts, bright and dark, banding the disk halfway to the poles. Their behaviour, however, indicates in them no regard for the sun, as they are quite oblivious both to the planet's day and to his year. They last indifferently through both, and disappear at their own good time. That the brighter are clouds and the darker the gaps between seems inferable. But they are not as our clouds. With us the heat that causes cloud comes from without; with Jupiter from within. Sun-occasioned the one, self-evolved the other. We have visual evidence of this internal heat of Jupiter in the cherry-red that tinges his darker belts as if we there looked down into the seething cauldron below. We have theoretic proof of it, too, in the oblateness the disk presents taken in connection with what we know to be the planet's mean density. In two articles shortly to appear in the *Philosophical Magazine* those who care for mathematics will find that heat alone enables Jupiter to keep his youthful figure, and furthermore that his shape shows him to consist of a comparatively small kernel wrapped in a huge husk of cloud. Even those who do not care for the oldest of the sciences must admit a certain grandeur in it when theory can thus plumb depths experiment may never fathom.

These belts have another peculiarity. Their several parts are travelling at idiosyncratic rates. With them it is a go-as-you-please race, in which each outruns or falls behind its neighbour. On this interesting subject we owe most to your fellow-countryman, Mr. Stanley Williams, who for some years has acted as timekeeper and referee of this Jovian family contest. In future he will have no mean rival in the photographic plate. Not that it sees as well, but that it may be measured at leisure by any investigator who likes.

There is one feature you will mark in the photographs which has had a long and eventful history. I refer to the great red spot. Detected in 1879, it lasted as such to within a few years Rather a long life for a hole in the clouds! Now, properly speaking, we see only the grave in which it lies buried, the oval shell it once occupied. But these same photographs were in a sense the means of bringing its cradle also to light. Sixty years ago, a cycle of Cathay, Sir William Huggins made a fine series of drawings of the planet, and on receiving the present pictures was struck by the resemblance of the two. In consequence he sent me prints of his. On scanning them, my eye was caught by an oval placed as the present one lies. Clearly it was the cradle prepared already for the great red spot twenty years in advance. He had been present before its birth, as he was present after its demise.

The third point we may mention in these photographs is their revelation of the equatorial wisps. Some years ago Mr. Scriven Bolton detected a most curious set of markings lacing Jupiter's bright equatorial belt. His discovery met with the usual approved disapprobation which has been the orthodox reception of astronomical advance since Galileo's time. Were a discovery to be hospitably hailed it would prove disconcerting to the discoverer, who would instantly suspect something wrong. Eventually the subject was referred to us for corroboration. This we were able promptly to secure. A singular phenomenon they proved to be, criss-cross filaments of shading traversing the belt from triangular spots at its edges, for all the world like the lacings of a sail that holds the bolt-rope to its spar. Though perfectly evident to the eye, we hardly hoped to catch them on a plate. Nevertheless, Mr. E. C. Slipher did, and innumerable other images of them have since been got by us; their pictures you will presently see for yourselves upon the screen. Why such peculiar rents should be torn in the planet's great cloud envelope we cannot yet explain, but further news about them has still more lately come to us from the planet to which we now pass, the great ringed planet Saturn.

In some respects Saturn is the most difficult of the three planets to photograph, certainly the most tiring. So faintly is it illuminated that what takes but two seconds for Mars, takes twenty or more for Saturn. To keep the image of the planet upon its guiding cross-wires for that length of time, with the nervous knowledge that any slip will be fatal, seems an eternity. Since sensations measure existence, it may be commended as a sure though not happy way to prolong one's life.

On the resultant images may be seen abundant detail. Cassini's division is there as large as life and somewhat broader, due to the difficulty of keeping it still; so also is the shading of the inner side of ring B, and the tones of the several portions of ring A. The ball appears finely, its belts standing out even more than to the eye, and the duskiness of its polar hoods being peculiarly pronounced. The shadow of the ball upon the rings is, of course, salient, and so is the shadow of the rings upon the ball. This much is evident at a glance, but there is more to be made out by him who examines closely.

If we consider the images of November 4, which happen to be mine, we shall notice a dark band below the rings where they cross the ball, and one which is but dusky above them. Now at this date both the sun and the earth were above the plane of the rings, as we see the image, the sun the higher; the sun's relative latitude being—

$$-12^\circ\ 18'$$

that of earth—

$$-11^\circ\ 4'$$

We saw in consequence the shadow of the rings A and B underneath the rings themselves. This accounts for the dark band below. What then was the dusky band above? It could not be the shadow of these rings, for the shadow could not fall on both sides of them at once, nor could it be seen above. A little consideration will reveal to us what this band was. Inside of ring B toward the planet lies the crêpe-ring C. It is a semi-transparent ring because its particles are widely scattered, instead of seeming solid like the outer rings where the particles lie closer together. Their constitution we owe to perhaps the greatest mind of the last century, your own Clerk-Maxwell. This, then, was the explanation: in the dusky band we were looking through the crêpe-ring on to its own shadow thrown upon the ball. Thus the crêpe-ring revealed its presence unmistakably, not by being seen, but by being seen through.

If now we compare these images of November 4 with those taken by Mr. E. C. Slipher on September 9 we note a marked contrast in the two fringes of shadow. This corroborates what we have just deduced, for at this time the relative positions of the sun and earth were reversed.

In the case of Saturn, we have as another interesting detail, the excellent instance it affords of contrast. From the bright equatorial belt, the most brilliant part of the whole picture, we notice a regular gradation of tints down to the faintest parts of the rings. For it is noteworthy that the dark belts of the planet are not so dark as these. This grading is particularly serviceable for being practically that of the eye. For the colour screen and plate used were such as to give us the light from that portion of the spectrum of which the eye takes greatest cognisance. The relative effect, therefore, on the plate is the same as on the retina.

Lastly, we come to what is one of the greatest triumphs of the whole process, the self-recording of the wisps of Saturn. It was in September that these wisps were first detected visually, independently, by my assistant, Mr. E. C. Slipher, and myself. Curiously enough they were suspected synchronously on the photographic images, and

on later ones were definitely seen. They counterpart almost precisely those of Jupiter, though of course in very faint replica. Here comes in the beauty of the photographic method. Instead of taking but a single image, twenty or more are taken one after the other on a single plate. Meanwhile the colour-screen is moved. Thus any detail in the image due to defect on the plate proclaims its origin by its singularity, and in the same manner the colour-screen betrays its self-written markings. If a detail is repeated on several images in place it must be real, however faint.

As we take our leave of Saturn let me point out the beautiful elliptical figures of the rings thus shown, a symmetrical correctness wonderfully pleasing to the eye, and which the best of drawings fails to reproduce.

From the detail these photographs have thus proved themselves able to depict, they mark a new departure in planetary research. While, on the one hand, they exhibit to the world at large something of the advance recently achieved in our knowledge of the solar system; on the other, they constitute in themselves the beginning of a set of records in which the future of the planets may be confronted with its archived past, and which shall endure after those who first conceived such registry shall have long since passed away. They can never take the place of first-rate visual observation, but they will form a firm foundation for whatever shall subsequently be seen, and will enable such changes as must inevitably ensue to be the better collated and compared. They are the histories of the planets written by themselves, their autobiographies penned by light; and in their grand historical portrait gallery, where the planet's pasts live on for ever in immortal youth, astronomers yet to come may see the earlier stages of the great cosmic drama which is slowly but surely working itself out.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 30th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Chemical Dynamics of Serum Reactions.*" By Captain A. G. MCKENDRICK, I.M.S.

1. Amboceptor and complement are opposed in their actions on the cell, with the proviso that the former acts as a catalyst to the latter.

2. Complement action is lytic; amboceptoral action is primarily polymerising, or, as the case may be, agglutinative, and secondarily catalytic to complement.

3. The relation of these substances is expressed by the Law of Mass action, in the form—

$$\frac{dz}{dt} = \frac{y}{c}\left(\frac{x}{cz} - z\right) - \left(\frac{y}{c} - z\right)^2.$$

4. When the substance acted upon is in sufficient quantity this expression describes all serum reactions, viz., hæmolysis, bacteriolysis, opsonin, and stimulin reactions, agglutination, precipitation, and toxin action.

5. Toxins are compound, and consist of amboceptor and complement.

"*Method of Measuring Colour-sensations by Intermittent Light, with Description of an Unfinished Apparatus for the Purpose.*" (Preliminary Note). By GEORGE J. BURCH, M.A., F.R.S.

Briefly, the new method of measuring colour-sensations is as follows:—

A series of flashes of monochromatic light produced by a real induction a condition of colour-blindness in a small area of the field of view, which they surround, but do not invade.

This small area is occupied, also in flashes properly timed and proportioned, by the part of the spectrum under examination. The colour corresponding to that of the monochromatic flashes is, as it were, wiped out of it, and the observer sees the boundaries of the underlying colour-sensations as long as the flashes succeed one another at the proper rate.

"*Variation and Adaptation in Bacteria, Illustrated by Observations upon Streptococci; with Special Reference to the Value of Fermentation Tests as Applied to these Organisms.*" By E. W. AINLEY WALKER, M.D.

Numerous attempts have been made to differentiate and to identify varieties of bacteria by means of chemical reactions produced by them in special culture media. One of the most interesting of these attempts was that made by Gordon to prove the existence of definite varieties among streptococci by the use of certain test media.

Gordon and those who followed him believe that they can thus subdivide the streptococci into a number of fixed and independent varieties, and classify them into what Andrewes and Horder have spoken of as "provisional species." Their conclusions, however, could only be accepted were it proved beyond question that the reactions on which they rely are stable in character and exhibit constancy.

In the present communication evidence is adduced from an extended examination of particular strains of streptococci that the reactions concerned are by no means constant. Under the conditions of ordinary cultivation in agar jelly, and still more under culture in the environment supplied by special media, particular strains of streptococci are shown to exhibit wide variations in their reactions to Gordon's test media.

Thus it occurs that strains which are at one time totally different in their test reactions may at another time be found to be identical. Further, it appears that after suitable manipulation particular strains may be made to assume the characters now of one, now of another, of the types supposed to be differentiated by Gordon's tests.

The conclusion drawn is that no evidence exists of any fixed or specific differences among streptococci pathogenetic for Man, but that the differences observed are due to merely temporary and casual variations in the metabolism of these micro-organisms which thus readily adapt themselves to changed environment. Accordingly it is quite possible that suitably selected tests may be made to afford some valuable indication as to the probable habitat or recent environment of any given strain of streptococci.

"*Interrelations of Genetic Factors.*" By W. BATESON, F.R.S., and R. C. PUNNETT.

"*A Case of Gametic Coupling in* Pisum." By PHILIPPE DE VILMORIN and W. BATESON, F.R.S.

"*Gametic Coupling and Repulsion in* Primula sinensis." By R. P. GREGORY.

PHYSICAL SOCIETY.

Ordinary Meeting, March 24th, 1911.

Prof. H. L. CALLENDAR, F.R.S., President, in the Chair.

AN exhibition of a Sensitive Thermo-regulator and some Experiments on the Measurement of Electrolytic Resistance using Alternating Currents, were shown by Dr. H. F. HAWORTH.

The "thermo-regulator" consists of a toluene thermometer with mercury platinum contacts in a capillary tube; these contacts operate, through a Siemens telegraph relay, an electromagnetic switch, which cuts in or out the heating circuit. On account of the very small current required to operate the relay a fine capillary may be used, so ensuring a high magnification with low thermal capacity.

This paper was discussed by Messrs. LOWRY, F. E. SMITH, and WHIPPLE.

Experiments were also shown illustrating the ease with which a bridge containing an electrolytic cell could be balanced by placing a variable self induction in series with the cell and adjusting it and the resistance of the bridge simultaneously, as in Wien's experiments, except that a vibration galvanometer was used in place of the optical telephone originally employed by Wien.

The author's deduction from his experiments, that the resistance of an electrolyte varies with the frequency of the alternating E.M.F. applied, was discussed by Messrs. Campbell, Duddell, Lowry, F. E. Smith, and the Secretary.

A paper on the "*Oscillatory Currents in Coupled Circuits*," was read by Prof. G. W. O. Howe.

A demonstration was given by means of a double projection oscillograph of the currents in coupled oscillatory circuits. Each circuit consisted of a condenser, an air-core choking coil, and a strip of the oscillograph.

The condenser in the primary circuit was charged and discharged by means of a commutator on the spindle of the oscillograph motor. The two circuits may be taken to represent the condenser circuit and the aerial of a wireless telegraph sending apparatus, the frequency being two or three hundred instead of a million. The currents in the two circuits can be studied, and every change due to a variation in the damping of either circuit or in the coupling between the two circuits can be followed. This was illustrated by a series of typical photographic records.

A third oscillatory circuit may be taken to represent a wave-meter, and used to plot resonance curves, from which the damping can be calculated, as is commonly done in radio-telegraphic work. Here, however, we have the great advantage of knowing the damping accurately, and thus being able to check the resonance curve results under various conditions.

By altering the connections the conditions of the quenched spark sending apparatus, as used by Max Wien, Lepel, &c., was represented. Here the primary circuit is opened at the first moment that all the energy has been transferred to the secondary circuit, and no further beats or spark-gap losses occur.

Results were given showing that the oscillograph can be used to find the losses in condensers at various frequencies by discharging the condensers through inductances of known resistance.

Some Radio-telegraphic Apparatus in use at the City and Guilds College was briefly exhibited by Prof. G. W. O. Howe.

The wireless telegraphic receiving apparatus was shown connected up to the aerial, which is 260 feet high.

A transformer specially designed for experimental work at long wave-lengths was shown. By means of a Brown telephone relay and special trumpets fitted to the telephone receiver, the time signals and messages sent out from Norddeich and from the Eiffel Tower can be plainly heard anywhere in the lecture theatre.

The various types of receiving apparatus in use at the College were shown.

Owing to lack of time the discussion on these two papers was omitted.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, April 3rd, 1911.

Mr. E. Grant Hooper in the Chair.

The following papers were read and discussed :—

"*Measurement of High Temperatures.*" By C. T. Heycock, F.R.S.

The author referred to the early pyrometer of Wedgwood, Deville and Troost's iodine thermometer, and other such appliances, and indicated their inherent errors. He also referred to the practical difficulties attending the use of the gas thermometer and of calorimetric pyrometers. He then referred to more modern methods, such as those dependent on (1) the alteration of resistance of a wire, (2) the alteration of the electro-motive force of a thermo-couple, and (3) radiation methods.

Siemens appears to have been the first to use an electrical resistance pyrometer in 1871. Callendar re-investigated this method of pyrometry, and constructed improved apparatus with compensating leads. The accuracy of his formula connecting the alteration of resistance with temperature has recently been demonstrated by the use of the air thermometer up to a temperature near the melting-point of platinum.

The use of thermo-junctions of platinum, platinum-rhodium ; copper, constantan ; or iron, constantan, was referred to as giving a rapid determination of temperature accurate enough for most purposes. Certain difficulties attending their use were alluded to.

Radiation pyrometers which may be used outside the furnace, of which Féry's is the best known, were then described. This is now largely used for measuring the temperature of baths of molten steel.

Greenwood's determinations of the approximate boiling-points of metals, such as antimony, bismuth, chromium, and copper, by an optical method, were mentioned.

"*Gum from* Bombax malabaricum." By P. P. Phillips.

The *Bombax malabaricum* (vernacular name, *semul*), the red silk-cotton tree, is a large tree belonging to the *N. O. Malvaceæ*, and is found in the plains of India and the sub-Himalayan tract up to a height of 3500 feet, and in other parts of Asia and in North Australia.

It yields a gum which exudes only from the portions of the bark which have been injured by decay or by insects. This gum is a white opaque viscous mass, which readily turns red, and finally dries into hard brittle mahogany-coloured tears. It is known in the vernacular as *mocherus*, and from its astringent properties is largely used in India as a medicine. The gum contains about 8 to 9 per cent of mineral matter, chiefly sand.

Various qualitative reactions are described which show that the gum contains a considerable quantity of tannin. It yields red substances on hydrolysis with dilute acid, one of which, "*semul* red," possesses the colour of crimson lake. The investigation is being continued.

RÖNTGEN SOCIETY.

The Effects of Secondary X-Ray Radiation.

Ever since Prof. J. J. Thomson delivered the Address before the last meeting of the British Medical Association, in which he urged upon medical radiologists the value of the secondary homogeneous radiation proceeding from metals placed in the primary beam of the X-ray tube, a number of physicists on the one hand, and medical men on the other, have been devoting themselves to this problem. The pioneer in these investigations is Prof. C. G. Barkla, of King's College, London, and therefore more than an ordinary degree of interest attached to his Address on this subject before the Röntgen Society at its meeting on April 6th. After pointing out the value of the very soft or easily absorbed radiations obtained in this manner—radiations which have little influence in the primary beam from the tube when directed upon the tissues, because they are absorbed in the glass on their way out—he drew a distinction between the secondary radiation and the residue obtained after passing the beam through a filter. In the case of filtration there were non-homogeneous primary rays as well as homogeneous secondary ones. To obtain the pure secondary radiation one must use the radiation proceeding from the *surface* of incidence—*i.e.*, the metal plate or other substance—and that alone. There were three kinds of secondary radiation, he continued. The first was the scattered radiation proceeding from air

and from light gases, such as carbonic acid gas, nitrous oxide, and sulphuretted oxygen. The simple effect of scatter was common to the radiation from all elements of low atomic weight, and compounds containing the lighter elements. Another type of radiation was the corpuscular, equivalent to the β-radiation of radium, but by no means so practically available. The X-ray being electro-magnetic in nature, it followed that all substances—all heavy substances, at any rate—when exposed to them emitted this peculiar quality of radiation, but the distance to which these secondary corpuscular rays proceeded was infinitesimal—one centimetre in air and perhaps one-thousandth of a centimetre in water. The most important of these types, however, was that to which he gave the name of secondary fluorescent radiation. If one of the heavier gases containing bromine or iodine, or a plate of copper, zinc, lead, or iron, were placed in the path of the primary X-ray beam, the effect, shown by means of the leak in an electroscope, was very much greater than that of the scattered radiation. The fundamental distinction of this secondary radiation as compared with the primary was its almost entire homogeneity. To produce it the essential condition—a law which also held good in the fluorescence of ordinary light—was that the primary beam should be of a more penetrating type than the secondary radiation characteristic of the particular element. If a soft radiation from a tube were made to fall upon a lead plate, for example, no lead radiation would be excited. The lead must be exposed to harder rays than those which were characteristic of its ordinary stream. Every element, said Prof. Barkla, had its own characteristic radiation, and, indeed, without much hyperbole, it might be said that every element had its own particular spectrum, and gave off its characteristic lines, only, instead of plotting wave-lengths, it was necessary to plot absorbability. Some of his findings may be given :—

Secondary radiation from—	Thickness of aluminium to absorb half.	Thickness of water to absorb half
Copper ..	1/160th cm.	1/14th cm.
Silver . ..	1/10th ,, (also 1/2800th)	1·4 ,,
Antimony .	1/47th ,, (also 1/1700th)	3 ,,

Water being practically equivalent in this respect to the human tissues, the second column furnished a guide to the choice of a metal producing a secondary radiation to the required depth. As to the effects in the transforming substance itself, if a great degree of ionisation were required, a substance must be employed having the heavier atoms. It was useful to remember, added Prof. Barkla, that three factors were in absolute relation, and stood and fell together, namely, the absorption of the primary beam, the ionisation produced in the absorbing substance, and the secondary radiation emitted from that absorbing substance.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliv., No. 7, February 13, 1911.

Dehydration of Salts.—Lecoq de Boisbaudran.—By the action of a stable magnesium sulphate the quadratic sulphate of copper containing $6H_2O$ can be transformed into the sulphate with $5H_2O$. Moreover, orthorhombic cobalt sulphate ($7H_2O$) gives the hexahydrated salt, and a similar change occurs with the sulphate of nickel containing $7H_2O$.

Direct Etherification by Catalysis. Preparation of Benzoic Ethers.—Paul Sabatier and A. Mailhe.—In presence of a catalysing oxide, MO, a mixture of vapours of an alcohol and an acid can either yield a ketone, according to the equations—

$$MO + 2(R.CO.OH) = H_2O + (R.CO.O)_2M$$
$$= H_2O + MO + CO_2 + RCOR,$$

or an unstable salt which may then be decomposed giving ethylenic hydrocarbon or ether salt ;—

$$MO + 2(C_nH_{2n+1}OH) = H_2O + M(OC_nH_{2n+1})_2,$$
$$M(OC_nH_{2n+1})_2 = MO + H_2O + 2C_nH_{2n},$$

or—

$$M(OC_nH_{2n+1})_2 + 2(R.CO.OH) =$$
$$= MO + H_2O + 2(R.CO.OC_nH_{2n+1}).$$

In certain cases the first two reactions may be negligible, and the ether salt may be the sole product. Thus, with benzoic acid and primary alcohol, thoria being used as catalyser, a good yield of ether can be obtained. Isopropyl benzoate and cyclohexylbenzoate can be isolated in the same way, and similar results are obtained with the toluic acids.

Effects of Ultra-violet Rays.—A. Guntz and J. Minguin.—The ultra-violet rays emitted by a mercury lamp have a corrosive action not due to heating on crystals of benzylidene camphor. They decompose cane-sugar into dextrose and lævulose, and cause the polymerisation of indene. Yellow phosphorus is converted by them into the red variety, and crystalline sulphur becomes opaque and insoluble in carbon disulphide.

Action of Ultra-violet Rays on Linear and Cyclic Organic Compounds.—Daniel Berthelot and Henry Gaudechon.—Linear organic compounds are decomposed by the ultra-violet rays, but substances belonging to the aromatic series (*i.e.*, those containing cyclic nuclei) are unchanged by them. When side-chains are attached to the cyclic nuclei ultra-violet light has a slight action on them ; thus cinnamic acid is decomposed with evolution of carbon dioxide. The ultra-violet rays have no effect upon many metallic salts in aqueous solution (gold chloride, silver, or uranium nitrate, &c.), but ferrous sulphate readily gives a precipitate. Ferric sulphate is not affected except in presence of nickel or cobalt sulphates, when it gives a precipitate.

New Anhydrous Selenites.—R. L. Espil.—When a metallic oxide is heated in a sealed tube with a large excess of selenious anhydride to the melting-point of the latter, an amorphous anhydrous selenite is formed, if the metallic oxide is strongly basic. Other oxides, such as SnO_2, ZrO_2, ThO_2, are not attacked. The author has thus prepared the selenites of Cu, Ni, Co, Ce, Pd, Nd, La, Sm. The selenites of Pd, Nd, La, Sm are soluble in solutions of selenious acid, giving acid selenites, and this property may be employed to separate the oxides of these metals from those of Ce and Th.

Pyrogenation of Silver Nitrite.—Marcel Oswald.—When silver nitrite is heated it decomposes quantitatively according to the equation $NO_2Ag = NO_2 + Ag$. Two secondary reactions occur, viz. :—

$$N_2O_4 + Ag \rightarrow NO + NO_3Ag,$$
$$NO_2 + NO_2Ag \rightarrow NO + NO_3Ag.$$

The second of these has not been detected previously. The author finds that by varying the experimental conditions he can produce one or other reaction at will.

Ketones Derived from Phenylpropionic Acid.—J. B. Senderens.—When thoria is used as catalyser, phenyl propionic acid gives with fatty acids three ketones, one mixed and two symmetrical :—

$$3C_6H_5—CH_2—CH_2—CO_2H + 3RCO_2H =$$
$$= C_6H_5—CH_2—COR + (C_6H_5—CH_2—CH_2)_2CO +$$
$$+ RCOR + 3CO_2 + 3H_2O.$$

When the proportion of fatty acid is increased, only a very small amount of symmetrical aromatic ketone is formed. The author has prepared by this reaction the ketones derived from mixtures of phenyl propionic acid with acetic, propionic, butyric, isobutyric, and isovaleric acids. They are all colourless liquids with agreeable odours. Their oximes are oily substances, except that of benzyl acetone, which crystallises in needles.

THE CHEMICAL NEWS.

Vol. CIII., No. 2682.

A PHYSICO-CHEMICAL STUDY OF MERCURY SODIUM ALLOYS OR SODIUM AMALGAMS.*

By ERNEST VANSTONE (B.Sc., Wales), 1851 Exhibition Research Scholar, University College of South Wales and Monmouthshire.

Numerous investigations on sodium amalgams have already been carried out, and the literature on this subject has become very extensive. The greater part of this refers to dilute liquid amalgams containing small quantities of sodium. Comparatively little work has been done on the solid amalgams. An excellent *résumé* of the work up to 1904 is given in Abegg's "Handbuch der Anorganischen Chemie," vol. ii.

From all the investigations the conclusion is drawn that several compounds of sodium and mercury exist. The number and composition of these compounds, however, are not known with certainty. Below is given a list of the formulæ suggested by various investigators.

Author and reference.	Compounds formed.
Berthelot (*Ann. Chim. Phys.*, 1879, v., 18.442)	$NaHg_5$, $NaHg_6$.
Guntz and Ferée (*Comptes Rendus*, 1900, 131, 182) ..	$NaHg_4$.
Kerp and Böttger (*Zeit. Anorg. Chem.*, 1901, xxv., 1)	$NaHg_5$, $NaHg_6$,
Maey (*Zeit. Phys. Chem.*, 1899, xxix., 119)	$NaHg_5$, $NaHg_2$, NaHg, Na_3Hg.
Kurnakow (*Zeit. Anorg. Chem.*, 1900, xxiii., 434) ..	$NaHg_5$ or $NaHg_6$, $NaHg_2$, NaHg, Na_3Hg.
Schüller (*Zeit. Anorg. Chem.*, 1904, xl., 385)	$NaHg_4$, $NaHg_2$, $Na_{12}Hg_{13}$, NaHg, Na_3Hg_2, Na_5Hg_2, Na_3Hg.

The need of further investigation is obvious. It is well known that the ordinary valencies of the metals are not exercised in metallic compounds, and no satisfactory explanation of the nature of the union has been put forward. It was thought that an investigation of the specific volumes might throw light on this problem.

A dissertation has recently appeared by Bornemann ("Metallurgie," 1909), in which it is stated that the only methods for fixing with certainty the composition of these metallic compounds are those commonly employed by metallographers, namely :—

1. The investigation of the thermal diagram.
2. The study of physical properties other than freezing-points.
3. The preparation and examination of micrographs.

All three methods have been employed in the present work.

The Investigation of the Thermal Diagram.

Preparation of the Alloys.—The method of preparing sodium amalgams commonly employed, namely, by plunging pieces of sodium under mercury, is unsuitable and unnecessary.

Kurnakow melted sodium in a weighed retort, through which a stream of dry hydrogen was passing. A sufficient quantity of sodium was then poured off into an iron cylinder containing a little molten paraffin, and the retort was again weighed. The requisite quantities of mercury were then added to the sodium.

Schüller cut up the sodium under anhydrous ether and transferred it to a weighed crucible containing vaseline oil. Mercury was then added to the molten sodium.

In the present work the sodium was melted in a current of dry carbon dioxide, and caused to flow into a tube which had been previously weighed, and which was also full of carbon dioxide. The apparatus is shown in Fig. 1. A stick of sodium was placed in A, and the tube heated with a Bunsen burner until the sodium melted; on slightly diminishing the pressure in B the clean metal entered, leaving a shell of oxide in A. When cool, B was quickly stoppered and weighed. The stopper was then replaced by another of rubber, trebly bored. Through the wide central hole a glass tube, closed at its lower end, was passed.

This tube contained the thermometer, and also served as a stirrer, the rubber stopper allowing sufficient freedom of movement.

This mode of stirring was found necessary, owing to the fact that the amalgams adhere to glass and render it opaque. Through the other holes inlet and exit tubes for

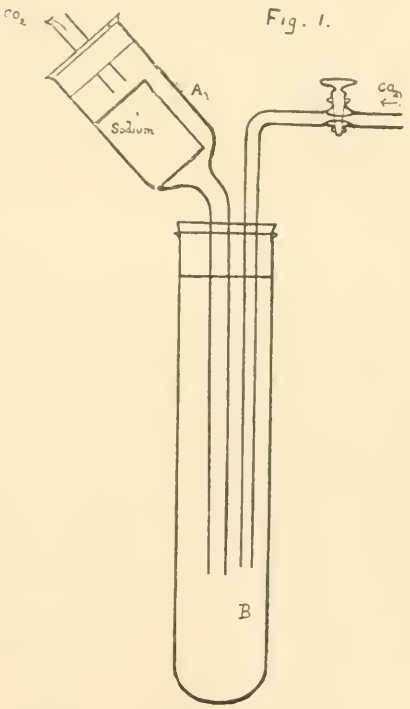


Fig. 1.

carbon dioxide were passed, the former being provided with a stopcock, the latter also serving for the introduction of mercury.

This was added from a small burette, which was weighed before and after. In preparing amalgams in this manner the sodium must be fused and the mercury added at first in small quantities; later, it may be added in large quantities, provided the alloy is kept molten.

(For ordinary purposes amalgams of all concentrations can be prepared as follows:—The badly oxidised surfaces of a piece of sodium are removed, and the sodium then dropped into ether containing traces of alcohol; ordinary methylated ether diluted with a large quantity of light petroleum answers very well. In a few minutes the sodium becomes quite bright; it is removed and immersed in molten paraffin contained in a crucible or test-tube, heated to 100° C., and the requisite quantity of mercury then added).

* A Paper read before the Faraday Society, March 14, 1911.

Fig. 2

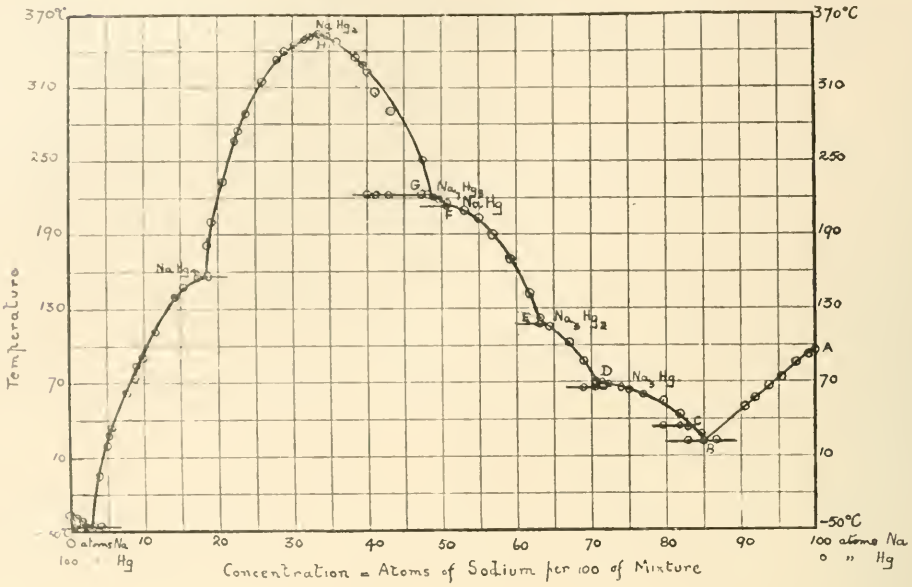
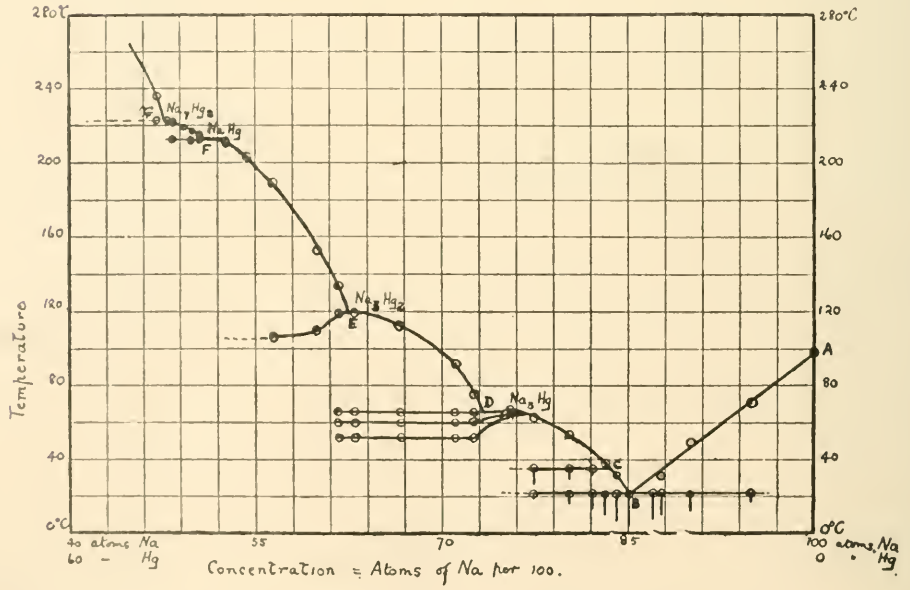


Fig 3.



Determination of the Freezing-points.—It will be shown later that the freezing-points extend over a very wide range of temperature, namely, from −47° C. to +360° C.

The heating arrangement for temperatures up to 250° C. consisted of a very large boiling-tube filled with olive oil, provided with a stirrer, and illuminated from behind by means of an incandescent burner. For temperatures between 250° C. and 360° C. the tube was heated in a bath of fusible alloy.

For temperatures below 0° C. the tube was placed in a boiling-tube containing light petroleum, and the latter cooled in a vacuum vessel containing a mixture of solid carbon dioxide and alcohol. The alloy was heated until entirely liquid, then allowed to cool slowly, meanwhile being vigorously stirred. The temperature was read every minute or half minute. In nearly all cases superfusion was observed, and the points determined are the maximum temperatures reached after over-cooling. The thermometers used were small Anschütz normal thermometers, each having a range of 50° C. and graduated in fifths.

Temperatures below 0° C. were determined with a pentane thermometer graduated in degrees. These thermometers were previously standardised. Corrections for the exposed stem were obviated as far as possible, as these

thermometers passed entirely into the experimental tube, and the latter was well immersed in the oil-bath. At the highest temperature obtained the correction did not exceed 1° C. The amalgam concentrations and temperatures of solidification are given in Table I. Throughout the work the former are expressed in atoms of sodium per 100 atoms of the mixture.

The cooling curves of some of the alloys showed a second arrest. This is given under T_2 in the table.

Table I.

No.	Conc.	T_1 (°C.).	T_2 (°C.).
1	100	97·5	
2	99·86	96·8	
3	99·52	95·1	
4	99·25	93·8	
5	99·06	93·1	
6	97·7	86·1	
7	97·2	83·0	
8	95·35	76·2	
9	95·25	74·5	
10	93·6	67·8	
11	91·68	58·5	
12	90·47	51·4	
13	86·7	21·35	
14	84·8	27·2	21·4
15	83·4	32·6	21·4
16	81·8	43·0	34·9
17	79·67	54·2	34·4
18	79·24	55·2	34·4
19	76·74	60·0	
20	76·1	61·4	
21	75·0	63·9	
22	74·23	64·1	
23	73·91	65·4	
24	71·6	69·6	65·8
25	70·6	69·8	65·7
26	69·0	86·5	65·6
27	66·9	102·0	
28	64·3	115·1	
29	63·9	117·1	
30	63·2	120·9	116·7
31	61·7	142·1	
32	59·2	169·4	
33	56·8	189·6	
34	55·0	202·4	
35	53·1	208·0	
36	50·7	214·7	
37	50·71	218·4	212·2
38	49·77	217·7	
39	49·16	220·0	
40	49·1	219·6	
41	48·7	220·6	
42	48·4	220·8	
43	47·4	251·0	222
44	42·8	291·6	222
45	41·3	305·5	222
46	40·14	323·8	222
47	40·1	323·3	222
48	39·7	331·7	
49	39·5	328·8	
50	38·5	335·4	
51	35·88	347·5	
52	34·8	351·0	
53	33·4	353·6	
54	32·4	352·4	
55	31·8	350·4	
56	30·6	347·2	
57	30·26	345·8	
58	29·02	340·5	
59	28·10	333·4	
60	26·11	315·2	
61	24·03	288·5	
62	23·05	274·0	
63	22·50	267·2	

Table I. (*continued*).

No.	Conc.	T_1 (°C.).	T_2 (°C.).
64	20·7	234·2	
65	19·09	200·4	
66	18·84	182·4	156·2
67	18·34	156·2	
68	18·0	156·2	
69	17·6	155·4	
70	16·57	154·9	
71	15·4	148·2	
72	14·2	139·1	
73	12·49	122·2	
74	11·49	111·1	
75	10·97	105·7	
76	9·90	91·0	
77	9·03	83·5	
78	8·83	75·9	
79	7·71	62·9	
80	7·67	54·6	
81	6·03	33·5	
82	5·45	27·6	
83	5·18	22·3	
84	5·04	18·8	
85	4·12	−5·5	−46·8
86	3·30	−46·8	
87	2·76	−46·8	
88	2·38	−46·8	
89	1·77	−42·8	−46·8
90	1·42	−42·3	−46·8
91	1·17	−40·8	
92	0	−38·6	

Discussion of the Freezing-point Diagram.

The concentration-temperature diagram obtained by plotting the above results is shown in Fig. 2. It contains nine branches. Starting with pure sodium at A, addition of mercury causes a lowering of the freezing-point until the eutectic-point B is reached. This occurs at a concentration of 85·2 per cent sodium, the eutectic temperature being 21·4° C. Further addition of mercury produces an elevation of freezing-point due to the formation of the compound Na_3Hg. On either side of B alloys show the second freezing-point, namely, that of the eutectic 21·4° C. At the point C, concentration 83·4 per cent sodium, the freezing-point is 34·4° C. The cooling curves of alloys in the neighbourhood of C, but containing larger proportions of mercury, show three arrests, the first being above 34·4° C., the second 34·4° C., and the third 21·4° C. The temperature 34·4° C. appears to be that at which the compound Na_3Hg undergoes a polymorphic change with evolution of heat. The initial freezing-points continue to rise as the percentage of mercury increases, reaching the maximum temperature of 353° C. at a concentration of 33·3 per cent sodium. Five new phases appear in the construction of this portion of the diagram. There are probably five different compounds of sodium and mercury. It is, however, difficult to decide the composition of these compounds with certainty, as the breaks in the diagram do not occur at concentrations which allow us to assign simple formulæ to these compounds, except in the case of $NaHg_2$, which occurs at a concentration of 33·3 per cent sodium. The temperatures, concentrations, and probable formulæ of the other phases are given in Table II.

The results obtained by Kurnakow and Schüller are given for comparison (Table II.). The portion of the diagram to the left of the maximum point is simpler. The freezing-points now fall with great rapidity as the mercury concentration increases. Two breaks occur—the first at a concentration of 18 per cent sodium and at a temperature of 156° C.—this is probably the compound $NaHg_4$; the second occurs at a concentration of 2·7 per cent sodium, and at a temperature of −41·6° C., a few degrees below the freezing-point of pure mercury; this is the eutectic-point due to the lowering of the freezing-points of mercury by the addition of sodium.

TABLE II.

Conc.	Temp. °C.	Phase.
100·0	97·5	Sodium.
85·2	21·4	Eutectic.
83·4	34·4	Transformation temperature.
71·7	65·7	Na_3Hg.
63·3	118·5	Na_3Hg_2.
51·5	212·2	NaHg.
47·6	221·6	Na_7Hg_8 (?).
33·3	353·5	$NaHg_2$.
17·9	156·2	$NaHg_4$.
2·7	46·6	Eutectic.
0·0	38·6	Mercury.
	Schüller.	
100·0	97·5	Sodium.
85·2	21·4	Eutectic.
84·1	33·9	Transformation temperature.
71·8	66·2	Na_3Hg.
61·9	123·0	Na_3Hg_2.
50·9	219·0	NaHg.
48·1	227·0	$Na_{12}Hg_{13}$ (?).
33·3	360·0	$NaHg_2$.
18·1	159·0	$NaHg_4$.
2·8	48·2	Eutectic.
0·0	38·6	Mercury.
	Kurnakow.	
100·0	96·45	Sodium.
85·05	21·25	Eutectic.
71·9	67·0	Na_3Hg.
50·6	209·7	NaHg.
47·6	218·0	—
33·26	346·0	$NaHg_2$.
17·95	155·0	$NaHg_5$ or $NaHg_6$.

It is obvious from Table II. that there is excellent agreement between the present work and that of Schüller. The temperatures now obtained are generally intermediate between those of Kurnakow and Schüller. The former used mercury thermometers graduated in tenths for temperatures up to 200° C.; for higher temperatures the thermometers were graduated in degrees. The latter also used mercury thermometers graduated in degrees above 10° C. The lower temperatures were determined with an alcohol thermometer or with a thermo-element.

Two reasons may be suggested for these temperature differences—(1) the uncertainty of the stem correction; (2) the effect of oxidation.

It has already been stated how these were obviated in the present work. The effect of oxidation is to shift the diagram to the left; *e.g.*, a break has been found at a concentration of 63·3 in the present work, whereas that of Schüller was at 61·9.

In the course of the work on the specific volumes in the liquid state described in the subsequent pages, a simple method of preparing sodium perfectly free from oxide was found. Consequently, I have re-determined the freezing-points of alloys containing from 100 per cent sodium to 48 per cent sodium, over which concentrations the greater number of changes occur. The sodium was drawn up into a pipette at a temperature of 130° C., using the apparatus in Fig. 5. The pipette was removed, quickly wrapped in cotton-wool, the lower end dipped beneath the surface of some liquid vaseline contained in the experimental tube, and the sodium allowed to run out of the pipette by opening the stopcock. The sodium thus obtained had not been in contact with air or moisture at any time, and presented an appearance similar to that of mercury. The presence of vaseline prevented adhesion of the metal to glass, consequently an ordinary stirrer of glass rod could be used. The thermometer also could be placed in immediate contact with the alloy, and removed and replaced by another when necessary. The alloys were made by adding mercury to the molten sodium as in former experiments.

The tube containing the alloy was heated in a large beaker of castor oil until the alloy was quite molten. It was then allowed to cool very slowly. The time during which the temperature of solidification remained constant was observed. In this way the horizontal and vertical lines of the thermal diagram, Fig. 3, have been obtained.

The results are given in Table III.

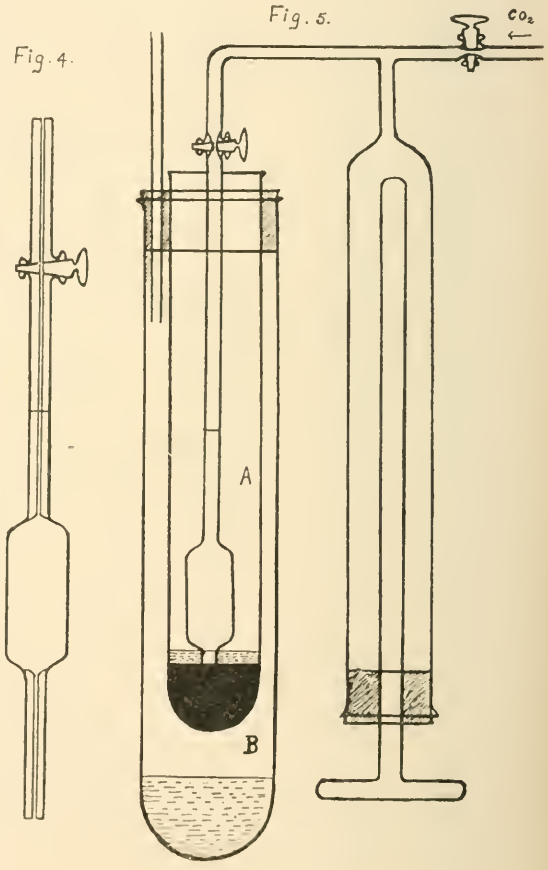
Fig. 3 is the thermal diagram obtained by plotting these results. It will be noticed that the eutectic horizontal at 21·4° C. extends nearly to the axis of temperatures on the right and to a concentration 75 per cent sodium on the left.

The horizontal through the transformation temperature 34·4° C. also extends to 75 per cent sodium on the left.

The second branch of the diagram has a maximum at 75·2 per cent sodium. These three facts prove conclusively that the compound Na_3Hg is formed.

Fig. 4.

Fig. 5.



The intersection of the second and third branches of Fig. 3 at the point D is now at a concentration of 73·9 per cent sodium. In the previous diagram, and also in that of Schüller, the point D was at 71·9 per cent. At a concentration of 71·4 per cent Schüller states that the compound Na_5Hg_2 is formed. Fig. 3 shows that this is erroneous.

The cooling curves of alloys containing from 75 to 63 per cent sodium show as many as three and four arrests. It appears that these solid alloys undergo polymorphic changes with evolution of heat. The horizontal through D also extends beyond 62·5 per cent, hence the formula Na_3Hg_2 has been assigned to the compound formed between D and E. Alloys along the branch E F show the

phenomenon of over-cooling to a marked extent at the second arrest, namely, in the neighbourhood of E. It was therefore not possible to find the duration of the transformation temperature.

Table III.

Concentration	Temperature of solidification. I. °C.	II. °C.	III. °C.	IV. °C.
100·0	97·6	—		
95·06	75·2	21·4		
89·99	49·2	21·4		
87·62	35·6	21·4		
87·03	—	21·4		
84·13	31·8	21·4		
83·26	37·7	21·4		
82·18	34·4	21·4		
80·20	53·9	34·4	21·4	
77·49	62·7	34·4	21·4	
75·55	67·0	64·8	64·2	
74·88	65·1	63·0	62·4	
72·65	75·6	65·5	60·5	52·0
72·51	77·6	65·5	60·5	52·0
70·57	91·8	65·5	60·5	52·0
66·73	113·2	65·5	60·5	52·0
66·48	113·6	65·5	60·2	52·0
63·04	119·4	65·2	60·2	52·0
61·70	134·2	119·0	65·2	60·3
60·05	152·2	110·0		
56·54	188·8	106·0		
54·26	203·8	—		
52·58	210·4	—		
50·52	214·7	212·8		
49·89	217·1	210·8		
49·27	219·2	207·4		
48·38	221·4	212·4		
47·88	222·1	—		
47·26	234·6	222·1		

The point F is at a concentration 51 per cent sodium, and the formula NaHg has been assigned to the compound produced along E F.

The next branch F G is very short; G is at a concentration 47·5 per cent sodium. In Schüller's diagram G is at 48 per cent sodium, and the formula $Na_{12}Hg_{13}$ is given; but this must be erroneous, as the transformation temperature 222·1° C. was constant for five minutes when the concentration was 47·26 per cent sodium, and four minutes when the concentration was 47·88. Schüller gives the temperature 227° C. The formula Na_7Hg_8 is now suggested. This requires the summit of the curve F G to be at a concentration of 46·66 per cent sodium.

In Table IV. the temperatures and concentrations at which the breaks occur are compared with those first obtained.

Table IV.

I. Concentration.	I. Temperature. °C.	II. Concentration.	II. Temperature. °C.
100·0	97·5	100·0	97·6
85·2	21·4	85·2	21·4
83·4	34·4	83·7	34·4
71·7	65·7	73·5	65·5
63·3	118·5	62·5	120·0
51·5	212·2	51·0	212·7
47·5	221·6	47·6	222·0

The agreement is good, especially the temperatures at which the changes of phase occur.

It may be concluded that six compounds of mercury and sodium are formed to which the following formulæ may be assigned:—Na_3Hg, Na_3Hg_2, NaHg, Na_7Hg_8, $NaHg_2$, $NaHg_4$.

(To be continued).

SEPARATION AND DETERMINATION OF COCAINE AND STRYCHNINE, AND ATROPINE AND STRYCHNINE WHEN THEY OCCUR TOGETHER.

By H. C. FULLER.

The alkaloids of the coca leaf and of nux vomica and of belladonna and nux vomica occur together as the active ingredients of certain classes of medicinal products, and it becomes necessary at times to determine how much of each is actually present. The groups follow each other so closely in their solubilities that no separation based on this property is possible, and one is obliged to employ other means.

It is a well known fact that the coca bases are readily hydrolysed by acids and by alcoholic potash, and a method for the determination of cocaine in a mixture of its allied alkaloids based on this phenomenon has been recommended by Garsed (*Pharm. Journ.*, 1903, p. 784). This chemist carries out the hydrolysis in alcoholic potash by heating for half-an-hour over the steam-bath, using a reflux condenser. It has been determined that the nux vomica alkaloids under these conditions are not changed, and hence a separation can be effected depending on this difference in behaviour.

A liquid drug product containing both cocaine and strychnine is first evaporated cautiously to drive off any alcohol, if present, and then quickly cooled to prevent the decomposition of the cocaine. If the material is a pill, tablet, or powder, it is ground up and digested with alcohol containing a little ammonia, the solvent filtered, and the treatment repeated twice more, the combined alcoholic solution being evaporated cautiously and the residue being taken up with dilute sulphuric acid and filtered if necessary. To the solution obtained by either of these methods, ammonia water is added in excess and the mixture shaken out three or four times with Prolius's mixture, reserving each portion of the solvent, and finally discarding the alkaline aqueous liquid. The solvent solution is then filtered, the filter-paper washed with more of the solvent, and the filtrate evaporated over the steam-bath, using a fan, care being taken to prevent the residue from being heated excessively. The resulting product is now dissolved in about 15 cc. of dilute sulphuric acid and the acid solution shaken out five times with chloroform, if caffein is known to be present; if not twice is sufficient. All the chloroform shakings are finally combined, washed once with water, and then the chloroform discarded and the wash-water added to the acid liquid. Ammonia is then added in excess and the solution shaken out three times with chloroform, the solvent solutions are combined, washed once with water, and the chloroform run through cotton, inserted in the stem of the separator, into a tared dish; two small portions of chloroform are then run through the cotton into the dish and the whole evaporated cautiously, using a fan, and the residue dried at 80° for a short time and then cooled in a desiccator and weighed. Cocaine being volatile, the drying must be at a low temperature. As the final portions of the chloroform evaporate, the dish should be rotated and removed from the steam to avoid spattering.

The weight thus obtained will give the combined cocaine and strychnine, or if the drug extract was present the combined coca bases with strychnine and brucine. The mixture is then dissolved in N/5 alcoholic potash, using 15 cc. for each decigrm. of cocaine supposed to be present, the solution poured into a digestion flask arranged with an air-tight stopper, the dish washed out with 10 cc. alcohol, and finally with 10—15 cc. water. The flask is then stoppered and placed over the steam-bath for one hour. At the end of that time the flask is opened, the contents poured into an evaporating dish, washing out the flask with alcohol and water, and evaporated until all the alcohol has been driven off. The residue is then transferred to a

separator, using water and chloroform, and the alkaline liquid shaken out three times with chloroform, collecting the solvent in another separator. The combined chloroform extracts are then shaken three times with 10 cc. portions of dilute sulphuric acid, the acid being reserved and the chloroform finally discarded. Ammonia is now added until in excess, and on cooling if much strychnine is present it will come out as a fine crystalline precipitate. The solution is shaken out three times with chloroform, the chloroform extract collected in another separator, washed with water, run through cotton into a tared dish, and the solvent evaporated. The dried residue will be found to consist of strychnine or strychnine and brucine.

This same general plan may be followed in separating atropine from the nux vomica bases. The tropeins are readily hydrolysed, and the strychnine and brucine can then be shaken out and finally purified according to the above method.—*Journal of Industrial and Engineering Chemistry*, ii., No. 9.

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.*

FIRST PAPER.—THE ANALYSIS OF NEODYMIUM CHLORIDE.

By GREGORY PAUL BAXTER and HAROLD C. CHAPIN.

Introduction.

INVESTIGATIONS bearing upon the rare earths have always been particularly attractive on account of some unusual chemical and physical properties of these substances, their peculiar relations to the Periodic System, and, in particular, the important position which some of them have taken with relation to artificial illumination. To be sure, any research involving the preparation of even one of the earths in a state of approximate purity is sure to be protracted, if not tedious. The very proof of the purity of a preparation is by no means easy to secure. The chief guides which have served in the determination of the purity of material have been the spectra, both absorption and emission, and the atomic weights. For a quantitative determination of purity the atomic weight is perhaps more frequently used than any other test. Hence, for this reason, as well as from theoretical considerations, an exact knowledge of the atomic weights of the rare earths is very desirable.

The atomic weights of certain members of the group have received a singularly large amount of attention. Those of cerium and lanthanum, for instance, have been investigated more times than that of iron. Yet owing to the unusual difficulties in the preparation of pure material, as well as to troublesome analytical problems, the determinations of the atomic weights of the rare earths are probably of a lower order of accuracy than those of the common elements.

Among the standard methods which have heretofore been employed in the determination of atomic weights of the rare earths, the following are the most important:—

The Analysis of the Oxalate (Stolba, *Sitzungsber. böhm. Ges.*, December, 1878).—The dried oxalate is analysed for the oxide by ignition, and for oxalic acid by titration with permanganate. The complete analysis of the salt is necessary on account of the invariable presence of an uncertain amount of crystal water even in the dried salt. Gibbs has pointed out (*Proc. Am. Acad.*, 1893, xxviii., 261), on account of irregularity in the water content, the necessity of grinding thoroughly the whole specimen of oxalate which is to be used for analysis, in order to insure homogeneity of material. Furthermore, it has been shown by Baxter and Griffin (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1684) and Baxter and Daudt (*Ibid.*, 1908, xxx., 563) that the oxalate must be precipitated in acid solution, since in neutral or alkaline solution the oxalates of the alkalis and ammonium are carried down by the rare earth oxalate in considerable quantities. Brauner (*Journ. Chem. Soc.*, 1902, lxxxi., 1266) has found that in some cases at any rate the oxalate hydrolyses in contact with water, although the magnitude of the latter error is doubtful. In spite of these difficulties the oxalate method is as easy to carry out as any, and probably the most satisfactory for approximate purposes.

The Analysis of the Sulphate.—The sulphates have been used for atomic weight purposes in several ways. Bahr and Bunsen (*Lieb. Ann.*, 1866, cxxxvii., 5) first employed the method of dissolving weighed amounts of oxide in sulphuric acid and weighing the sulphate after expelling the excess of acid. By the ignition of the oxalate it is doubtless possible to prepare the oxides in a very pure state if great care is taken to protect them from access to moisture or carbon dioxide, at any rate with elements which form trivalent compounds only. To prepare the sulphate in a neutral dry condition is a much more difficult proposition, owing to the retention of water and sulphuric acid if the temperature of heating is low, and to decomposition with loss of sulphuric acid at higher temperatures. The investigations of Bailey (*Journ. Chem. Soc.*, 1887, li., 683), Kruss (*Zeit. Anorg. Chem.*, 1893, iii., 46), Jones (*Am. Chem. Journ.*, 1902, xxviii., 31), Brauner (*Journ. Chem. Soc.*, 1902, lxxxi., 1248), Wild (*Ibid.*, 1904, xxxviii., 195), Brill (*Ibid.*, 1905, xlvii., 464), and Holmberg (*Zeit. Anorg. Chem.*, 1907, liii., 124) leave this matter still in a somewhat unsettled state.

The difficulty in obtaining the anhydrous sulphate in a neutral condition applies also to the method of ignition of sulphate to oxide. Furthermore, it is probable that the oxide prepared by ignition from the sulphate retains traces of sulphuric acid (Brauner, *loc. cit.*, 1263).

A third method depending upon the use of the sulphates involves the determination of the water in the octahydrated sulphate. Here the difficulty in obtaining crystals free from included cells of mother-liquor is superimposed upon that of insuring complete dehydration.

The Analysis of the Chloride.—The analysis of the chloride has been little used on account of the tendency for the formation of insoluble basic compounds during drying. As Matignon (*Comptes Rendus*, 1901, cxxxiii., 289; 1905, cxl., 1182) has pointed out, if the dehydration of the chlorine is conducted slowly and thoroughly enough in an atmosphere of dry hydrochloric acid gas, this difficulty disappears and a perfectly soluble product can be obtained, even after fusion. Hence, on account of the accuracy with which halogen salts may be analysed by precipitation with silver, this method is one of the best for atomic weight purposes. In testing the applicability of this method, we chose neodymium chloride for investigation, since neodymium compounds are comparatively easy to secure in an approximately pure state in large quantities. Furthermore, unlike its close relation, praseodymium, neodymium does not readily change from the trivalent state.

Historical.—The atomic weight of neodymium has already been determined many times, with discrepant results. This element and praseodymium, the other component of the old didymium, were first separated through the fractional crystallisation of the double ammonium nitrates by Auer von Welsbach in 1885 (*Sitzungsber. Akad. Wiss. Wien.*, 1885, xcii., 317). He determined their atomic weights by Bunsen's method of converting oxide to sulphate, but apparently interchanged his results in publication, as first suggested by Brauner, as he gave the value 140·8 for neodymium and 143·6 for praseodymium.

In 1898, Brauner (*Proc. Chem. Soc.*, 1898, xiv., 70; CHEMICAL NEWS, 1898, lxxvii., 161), by converting oxide to sulphate, obtained the result 143·6 for neodymium. In this he included a correction for an impurity of 2·9 per cent of the corresponding praseodymium compound, estimated by comparison of the intensity of absorption spectra.

In the same year Boudouard (*Comptes Rendus*, 1898, cxxvi., 900) obtained a neodymium preparation by precipi-

* *Journal of the American Chemical Society*, xxxiii., No. 1.

tation with potassium sulphate from some impure yttrium material. Apparently to identify the base rather than to establish its atomic weight, he analysed the sulphate by converting it to oxide, with the result 143·0. Undoubtedly his material contained praseodymium, as no steps were taken to remove this inevitable impurity.

In 1898 Jones (*Am. Chem. Journ.*, 1898, xx., 345) also investigated both neodymium and praseodymium with material purified by crystallisation as the double ammonium nitrate. Cerium and lanthanum were eliminated by precipitation as basic nitrates, and a correction for residual praseodymium was obtained by comparing the intensities of its absorption bands in the neodymium preparations with those of the same bands in dilute praseodymium solutions of known strength. The atomic weight was found by converting the oxide to sulphate. The average of twelve results, ranging in value from 143·46 to 143·62, was 143·55. Corrected for praseodymium content this value becomes 143·60.

In 1901, after further purification of his original material, Brauner published another determination (*Proc. Chem. Soc.*, 1901, xvii., 66), which yielded the value 143·89. As this is the result of but one analysis and includes a correction of questionable accuracy for praseodymium impurity, it can hardly be given much weight.

Auer von Welsbach (*Sitzungsber. Akad. Wiss. Wien.*, 1903, cxii., 1037), in 1903, published the results of further study of both neodymium and praseodymium. His source of material was a large quantity of double ammonium nitrates obtained as by-products in the technical extraction of lanthanum. A long series of fractional crystallisations as double ammonium nitrate served to free the neodymium from all but a trace of praseodymium. With this material, undoubtedly of very high purity, three analyses were made by the Bunsen method of converting oxide to sulphate, from which the atomic weight values 144·55, 144·52, and 144·57, respectively, were obtained. Unfortunately, no details of procedure are given.

A point of especial interest in connection with Jones's and Brauner's results is Auer's observation that the praseodymium absorption spectrum is weakened considerably by lanthanum and cerium ammonium nitrates and other salts, as well as by concentrated nitric acid, the effect of which was mentioned in Auer's earlier paper. Clearly any quantitative comparison of the intensity of the praseodymium spectrum from solutions of praseodymium salts alone, with that from solutions consisting mainly of other rare earth salt, is unreliable.

Feit and Przibylla (*Zeit. Anorg. Chem.*, 1905, xliii., 202) dissolved weighed amounts of various rare earth oxides in sulphuric acid and titrated the excess of acid, using methyl orange as the indicator. The end-point was interfered with by the pink colour of the neodymium salt, but this difficulty was obviated by comparing the solutions with standards containing the same amounts of indicator and neutral neodymium salt. Their neodymium material was prepared by fractional crystallisation of the double magnesium nitrate. This preparation showed no trace of the strongest praseodymium and samarium absorption bands, although the "hellblau" colour of the oxide was considered the best proof of its purity. The result for the atomic weight of neodymium was 144·60.

Holmberg (*Z. An. Ch.*, 1907, liii., 83), after a study of the rare earth salts of twelve organic acids, selected the meta-nitrobenzene sulphonate as particularly suitable for the purification of neodymium, and by one hundred and sixty-two series of crystallisations obtained thirteen fractions ranging in atomic weight from 144·0 to 145·3. The purest fractions were selected, and the oxide obtained by ignition of the oxalate was weighed and converted into sulphate. The value 144·10 was obtained as the mean of six results varying from 144·03 to 144·15.

The International Committee on Atomic Weights have chosen as the most probable value 144·3, which represents on average of the more recent determinations.

(To be continued).

CAST COPPER OF HIGH ELECTRICAL CONDUCTIVITY.*

By Dr E. WEINTRAUB.

THE production in the foundry of pure copper castings mechanically sound and possessing an electrical conductivity comparable to that of pure forged copper has been an important problem ever since the development of electrical machinery and apparatus. The literature as well as the patent files are replete with descriptions of methods for the accomplishment of this result. Secret compositions, warranted to give high conductivity copper, were and are being sold to foundrymen, and there are but few foundry foremen to be met with who do not claim to have some time or other obtained the desired result by adding "phosphorus" or similar material. Obstinately, however, the casting of high conductivity copper refused to make its entrance in the foundries and we may assume that there were good reasons for it.

The cause of the difficulty of producing sound pure copper castings has been sufficiently well understood for a long time. Molten copper has the property of dissolving gases such as oxygen and of setting a part of these gases free on cooling. This produces pin-holes and even big cavities. The casting obtained is therefore mechanically unsound and has naturally a low electrical conductivity.

The elimination of these dissolved gases presents but little difficulty. It is sufficient to add one of the well-known deoxidisers such as zinc, magnesium, phosphorus, &c., in small quantities to bind the oxygen chemically. Copper castings free from blow-holes are thus easily produced. The electrical conductivity of the copper thus produced is, however, as a rule, low; and this because all the *deoxidisers used had also the property of combining with copper*, and the remarkable rate at which the conductivity of copper drops when small amounts of impurities are alloyed with it is well known. The amount of oxygen dissolved in copper during the process of melting is a variable quantity and is distributed throughout the whole mass. It is therefore practically impossible to add the deoxidiser in such a way as to eliminate oxygen completely without, at the same time, alloying it to a certain degree with the copper. Accordingly the conductivity of the resultant product was a matter of accident. In the laboratory sometimes good results were obtained, but they were hard to duplicate and the transfer to the foundry was always a disastrous experiment.

It seemed to me that what was needed for the solution of the problem was the finding of a deoxidiser which would have no affinity for copper (at least at the melting point of the latter) and which, therefore, could be added in excess with impunity.

While carrying on the work of the isolation of the pure element boron, and its fusion, the lack of affinity of this element for copper has forcibly impressed itself on my mind. Boron has, at the melting point of copper, a great affinity for oxygen, nitrogen, &c., and it occurred to me, therefore, that boron ought to be the ideal substance for deoxidising copper.

Pure boron as prepared by methods described by me in paragraphs 2 and 4 of my article (*Trans. Am. Electrochem. Soc.*, xvi., 165) can by this time, be produced in large quantities and is rather inexpensive for uses based on its electrical properties. For casting copper, however, its price would probably be too high.

In the course of the investigation mentioned I had prepared, however, an amorphous powder which contained as essential impurity only a certain percentage of oxygen and which I termed "boron suboxide. This substance is prepared by a modification of the reduction-process of boric anhydride by magnesium. Obviously for the purpose of eliminating oxygen from copper without introducing any

* An Address read before the Chicago Meeting, American Electrochemical Society, October 13, 1910. From the *Journal of Industrial and Engineering Chemistry*, ii., No. 11.

impurity capable of alloying with copper, this boron suboxide would be as good as pure boron, or perhaps better on account of its being obtained in form of a very fine powder.

This substance was used in the first experiment. The very first attempt was successful. A perfectly sound bar was obtained with a conductivity of 94 per cent. 0·1 per cent of the weight of the copper was added. Further experiments showed that the amount of boron suboxide ould be reduced to one-thirtieth per cent, and also that the addition of a large excess, say of 1 per cent, did not diminish the conductivity or change in any way the mechanical properties of the cast copper.

Here was, therefore, a method which could be put into the hands of any foundry man and which would always give good results provided the copper (ingots or scrap) melted down was pure metal.

A further simplification could, however, be introduced into the process. The reduction of boric anhydride by magnesium, the first being in excess, gives a product containing magnesium borate, boric anhydride, and boron suboxide. While the last one is the active agent, the first two are harmless. In fact, the presence of boric anhydride and magnesium borate is even an advantage as the addition of a larger mass of material makes the operation easier; also the boric anhydride would probably dissolve the copper oxide and bring it to the surface as copper borate. It is therefore unneccessary to submit the direct product of the reaction to chemical treatment for the purpose of isolating the boron suboxide. It is sufficient to grind up the mixture into coarse grains and use an amount of it which contains the necessary amount of boron suboxide.

The foundry practice at present is to add 1 per cent to 1½ per cent of this material, which is equivalent to 0·08 to 0·1 per cent of boron suboxide.

The properties of the material obtained are as follows:—

The electrical conductivity obtained can be as high as 97½ per cent if the copper melted down is perfectly pure. In the foundry, where the scrap copper which is melted down cannot always be very carefully selected, a conductivity of 91 to 95 per cent is obtained, and a guarantee of 90 per cent is at present given.

The resultant casting is readily machined; fears which were entertained on this subject did not materialise, and the engineers using the material have not complained on this account.

The mechanical properties are as follows:—

Tensile strength.	Elastic limit.	Elongation.	Reduction in area.
24350	11450	48·5 per cent.	74·49 per cent.

Castings are being made of all shapes and sizes with no more difficulty than in the case of brass. Sand and iron moulds can be used, and for standard articles the latter are preferred.

The use of cast copper lies in two different directions—1. Replacing forged copper. In this case a great saving in cost is often obtained. (2) Replacing alloys of copper. The gain in conductivity allows the reduction in bulk and thus a saving in material.

The use of this material is spreading as the engineers get better acquainted with it and is already of very considerable magnitude. It is interesting to note that in spite of the fact that cast copper has lower conductivity than forged copper, in many cases, as for instance in case of current transformers, the effect of higher conductivity is obtained by substituting it for forged copper. This is due to the fact that in casting a chance is given to eliminate rivetted screws or soldered joints whereby a number of poor contacts are avoided. Not only this but the elimination of joints often insures a better operation.

The cost of the boron added is small; at the present prices of magnesium and boric anhydride the cost per pound of copper is less than 0·73 of a cent.

The success with "boronising" copper, as it is now called in the foundry, suggests new lines of work which I have taken up lately.

Among these I mention:

First, the addition of boron to different copper alloys.

Second, the replacing of the poling operation in the process of refining copper by a "boronising" operation.

In conclusion, I want to express my appreciation of the excellent work done by my assistant, F. A. Kroner, without whose energy and foundry experience the technical and commercial success of the process described would have been greatly delayed.

SELECTIVE OXIDATION.

By HARRY C. JONES and W. W. STRONG.

THIS is part of an investigation being carried out with the aid of a grant from the Carnegie Institution of Washington.

The power of solutions to absorb light enables us to distinguish between the parts of the dissolved salt combined with each solvent in a mixture of two solvents. If uranous bromide, obtained by the reduction of uranyl bromide with nascent hydrogen, is dissolved in a mixture of methyl alcohol and water we have two well-defined sets of absorption bands. One set is characteristic of the uranous salt dissolved in water and is what we term uranous "water bands." The other set is characteristic of the uranous salt dissolved in methyl alcohol, and we term these the uranous "methyl alcohol bands."

If we add certain oxidising agents which are soluble in both water and methyl alcohol, the portion of the salt combined with water is oxidised and the part combined with alcohol remains unchanged. This is shown by the fact that the "water bands" entirely disappear and the "alcohol bands" remain practically unchanged.

The experiment as actually carried out was the following:—To two parts, by volume, of a solution of uranous bromide in water was added one part of water and six parts of methyl alcohol. The absortion spectra of this solution showed the bands of the "hydrated" uranous bromide and the bands of the "alcoholated" uranous bromide. A small amount of sodium perchlorate dissolved in methyl alcohol was added to the above solution. Sodium perchlorate is, of course, soluble in both methyl alcohol and water. There was usually a small amount of hydrobromic acid present from the reduction of the uranyl to the uranous salt. This would, of course, liberate perchloric acid, which would be the real oxidising agent. The result is that the uranous "water bands" disappear, showing that the uranous salt, bromide or perchlorate, had been oxidised to the uranyl condition. The "water bands" that disappear have the following wave-lengths:—

λ 4850 λ 4970 λ 5500 λ 6420 λ 6750

The uranous "methyl alcohol" bands do not disappear, their intensities being practically the same as before the addition of sodium perchlorate. The more prominent of these bands have the following wave-lengths:—

λ 4900 λ 5020 λ 5260 λ 6220

An experiment was carried out which was similar to the above, but in which a different oxidising agent was used. Uranous bromide was dissolved in a mixture of methyl alcohol and water, and calcium nitrate dissolved in methyl alcohol was added to the solution, calcium nitrate being soluble in both of the above solvents.

In this case the "water" bands disappeared entirely, and the intensity of the "alcohol" bands was not diminished in the least. These oxidising agents, although soluble in both of the solvents present, are capable of oxidising the part of the uranous salt that is combined with water—the

hydrated salt—but are incapable of oxidising the part of the salt that is combined with alcohol—the alcoholated uranous salt. When hydrogen dioxide is used as the oxidising agent, both the "hydrated" uranous bromide and the "alcoholated" uranous bromide are oxidised to the uranyl condition. Selective oxidation is shown by calcium nitrate and by sodium perchlorate, but not by hydrogen dioxide.

Similar results were obtained with uranous chloride. When calcium nitrate is added to a solution of uranous chloride in a mixture of water and methyl alcohol, the "hydrated" uranous salt is oxidised and the "alcoholated" salt remains practically unchanged. When potassium chlorate is added to a solution of uranous chloride in a mixture of water and methyl alcohol, the absorption bands corresponding to the "hydrated" salt weaken very greatly in intensity, while the bands corresponding to the "alcoholated" salt do not show the slightest diminution in intensity. Potassium chlorate is only slightly soluble in methyl alcohol. Both the "hydrated" and "alcoholated" salt are completely oxidised by hydrogen dioxide.

The comparatively slow transformation of the "alcoholated" uranous salt into the "hydrated" salt is probably due to the presence of the uranyl ions in the water.—*American Chemical Journal*, xlv., No. 1.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 6th, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

"*A Chemically-active Modification of Nitrogen produced by the Electric Discharge.*" (Bakerian Lecture). By Prof. the Hon. R. J. Strutt, F.R.S.

The leading facts established are :—

1. That pure nitrogen, from whatever source, subjected at a low pressure to the jar discharge, undergoes some modification which causes it to glow for a short time after it has been sucked away from the discharge.

2. The glow which is emitted while the gas returns to its normal condition is not destroyed by the removal of ions. It is weakened by heating, intensified by cooling. This seems to favour the view that it is due to the recombination of dissociated atoms.

3. The modified nitrogen acts on ordinary phosphorus, combining with it, and at the same time forming much red phosphorus.

4. It combines with sodium and also with mercury at a gentle heat (say 150° C.), forming in the latter case an explosive compound, and in each case developing the line spectrum of the metal concerned. It also develops the line spectra of other metals, probably combining with them.

5. It develops the band spectra of compounds, when these are vapourised in it, giving in many cases spectra of substances too unstable to be examined at the temperature of the Bunsen flame.

6. It attacks acetylene, and substances like ethyl iodide or chloroform, setting the halogen free when there is one, and combining with the carbon to form cyanogen. This is proved by the brilliant cyanogen spectrum produced, and by direct chemical tests, such as formation of Prussian blue.

7. It attacks nitric oxide, with formation, strangely enough, of nitrogen peroxide, a more oxidised substance.

Papers were read as follows :—

"*The Association of Lead with Uranium in Rock-minerals, and its Application to the Measurement of Geological Time.*" By A. Holmes.

"*Dynamical Value of the Molecular Systems which emit Spectra of the Banded Type.*" By Prof. E. T. Whittaker, Sc.D., F.R.S.

It is now widely believed that when the spectrum emitted by a luminous body is of the banded type, the small vibrators which give rise to the radiation are the molecules of the substance, as distinguished from atoms or ions. This result is applied in the main body of the paper, in order to suggest a dynamical system, which is formed of two members in the same way as a diatomic molecule may be supposed to be formed of two atoms, and which has free periods of vibration related to each other by the same formula as holds in the case of banded spectra. This formula presents a certain peculiarity, in that the frequency of vibration occurs in it linearly; whereas in the equation for determining the free periods of dynamical systems in general, the frequency enters by its square. It is shown that from this peculiarity in the radiation of a molecule certain inferences may be drawn regarding the dynamical character of the connection between the atoms within the molecule. It is shown that a somewhat modified mechanism would emit radiations connected by the same law as that which Balmer found for the hydrogen lines.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 5th, 1911.

Mr. E. W. Voelcker, President, in the Chair.

Messrs. Joseph Clifford, James Connah, Harley F. Knight, Charles H. La Wall, William Rest Mummery, and W. Macro Seaber were elected Members of the Society.

A certificate was read for the first time in favour of Mr. Alfred Douglas Heywood, 73, High Street, Southend-on-Sea.

Certificates were read for the second time in favour of Horace G. Battye, George Davidson Elsdon, Norman Evers, and Arthur William Knapp.

The following papers were read and discussed :—

"*The Analytical and Microscopical Examination of Compound Liquorice Powder.*" By G. E. Scott-Smith and John Evans.

The authors have investigated compound liquorice powder, and have shown how its purity may be ascertained by microscopical examination.

"*Note on Almond and Apricot Kernel Oils.*" By Raymond Ross and Joseph Race.

The various constants for the oils and their fatty acids of two authenticated samples are given and their practical identity of composition is noticed.

"*Constants of Chicken and Turkey Fats.*" By Raymond Ross and Joseph Race.

The authors give a number of analytical constants for chicken fat and turkey fat.

"*Note on Gerber's 'Neusal' Milk Test.*" By John Golding.

The desirability of replacing the sulphuric acid in Gerber's milk test is pointed out. Investigations on the "Sinacid" and "Sal" methods indicated that a large proportion of alcohol was dissolved in the fat. Dr. O. Wendler's "Neusal" method makes use of the solvent action of sodium salicylate on butyl alcohol, and of the action which the resulting solution has on the milk. Good results were obtained when the correct quantity of butyl alcohol was used, but it is shown that the results vary if larger quantities of the alcohol are used, owing to the fact before mentioned of the solubility of the alcohol in fat from

the "Neusal" solution, which is, however, less than where alkali is used.

The author concludes that this additional error will outweigh the advantages which the new method possesses over the original acid Gerber test.

"*Note on Abnormal Cotton Cakes.*" By JOHN GOLDING.

Analyses are given of cotton cakes containing about 18 per cent of water. These cakes on keeping for a month were found to contain over 20 per cent, and on further keeping the moisture went up to over 30 per cent owing to decomposition. The analyses of the decomposed cakes show that the oil had undergone the largest proportion of decomposition; the carbohydrates also were largely decomposed. Bacteria have been isolated from the cakes, but the specific organism affecting the oil has not been identified. It is suggested that in cases of this kind where decomposition takes place some method of correction is necessary in order to estimate the original food constituent present in the sample.

"*A Further Contribution to the Question of Turpentine Substitutes.*" By J. H. COSTE and L. MYDDELTON NASH.

It is shown that large amounts of aromatic hydrocarbons are present in the fractions of Borneo, Roumanian, and other petroleums which are used as turpentine substitutes. The determination of flash-point (Abel), the frothing test, and fractional distillation are shown to be useful for the detection of adulteration and Armstrong's polymerisation method for determining the amount of adulterant present in mixtures.

NOTICES OF BOOKS.

A Course in Qualitative Chemical Analysis. By CHARLES BASKERVILLE, Ph.D., F.C.S., and LOUIS J. CURTMAN, Ph.D. New York: The Macmillan Company. 1910.

THERE is no special feature in this laboratory book of qualitative analysis to mark it out as different from or superior to the many which have issued from the press recently in answer to the demand created by the recognition of the value of analytical chemistry as a factor in mental training. On the other hand, the treatment of the subject, if unadventurous, is thoroughly sound, and the student who works through the book will get a full acquaintance with the principles of analytical chemistry. Emphasis is laid upon the quantitative side of qualitative work; thus the authors advocate the use of solutions of known strength. They follow the usual plan of stating the reactions of the metals in detail, by which a knowledge of the qualitative facts is instilled, and then outlining the method of analysis employed, and finally giving the scheme of separation. Notes are added pointing out the difficulties which may be encountered, and giving some additional information, and frequent allusions are made to the relative sensitiveness of the tests described.

Qualitative Chemical Analysis. By J. I. D. HINDS, Ph.D., LL.D. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1910

A FAIRLY advanced course of qualitative analysis is given in this book, which would be found more valuable as a work of reference to be kept in the laboratory for occasional use than as the sole guide for the routine work of the student, who would probably consider that it is rather full, and gives a bewildering mass of detail instead of making the main principles of analysis perfectly clear. The treatment of the subject is based upon the ionic hypothesis, and the law of Mass Action and the theory of electrolytic dissociation are fully discussed and freely applied. Modern analytical methods are included; for instance, the cobaltinitrite test for potassium and the separation of calcium and strontium by means of amyl alcohol, and the spectrum of each metal is briefly described.

The Literature of Medicine and Natural Science. London: J. and A. Churchill. 1911.

THIS catalogue of the publications of Messrs. J. and A. Churchill is an exceptionally useful guide to recent books on medical science, and contains details of the contents, price, &c., of standard works and new editions. The date of issue of each book is given, and specimen illustrations from the more important recent works are included, as well as excerpts from reviews. The catalogue is well worth the attention of our readers who are interested in medical publications.

"*Salvarsan*" *or* "606." By W. HARRISON MARTINDALE, Ph.D. (Marburg), F.C.S., and W. WYNN WESTCOTT, M.B. (Lond.), D.P.H. London: H. K. Lewis. 1911.

IN this book a full account is given of the chemistry of dioxy-diamino-arsenobenzol, or "Salvarsan," which has recently come into prominence as a substance possessing hitherto unheard of parasitotropic properties. Most of the work upon the subject has been done in Germany and the results published in German periodicals, and of these results an excellent analysis is given in this book, which is the first *résumé* on Salvarsan to be written in English. Ehrlich's work and that of Hata is discussed in full detail and the therapeutic uses of the substance, the dose to be employed, and methods of injection are all fully but concisely treated, and an unbiassed account is given of the results of the treatment, which, in some cases, can only be deserибed as extraordinarily satisfactory as well as rapid. The authors utter explicit warnings as to possible ill-effects and make no attempt to conceal cases of failure. The book also contains abstracts of articles on the subject which have been published in the *Lancet* and the *British Medical Journal*, and some authoritative communications from specialists who have had opportunities of testing the value of Ehrlich's preparation.

The Journal of the Municipal School of Technology, Manchester. Vol. III.

AT the present moment, when we are hearing and thinking a good deal about inducing a closer and more fruitful union between pure science and technology, it is interesting to read this record of the work of the teachers and students of an institution which is sending out into the world a supply of excellently trained students of the type which must inevitably bring about the hoped for union. The papers, most of which have been reprinted from scientific journals, testify to the admirable zeal and activity of the members of the teaching staff of the Municipal School of Technology, and show clearly what excellent results may be obtained from such institutions if well equipped and well arranged. The Report contains a list of all papers which were read either by students or teachers before meetings of learned societies during the year 1909.

Chemistry for Matriculation. By G. H. BAILEY, D.Sc. Lond., Ph.D. Heidelberg, and H. W. BAUSOR, M.A. (Price 5s. 6d.). London: University Tutorial Press, Ltd. 1910.

THE new syllabus of the London Matriculation Examination has necessitated the preparation of a fresh edition of this text-book, which has been thoroughly revised by Mr. H. W. Bausor for the purpose, and the opportunity has also been taken of making many alterations in the text.

Thus a considerable amount of experimental matter has been added and a section on the metals has displaced that on the Chemistry of Daily Life. The introductory section is particularly full and clear, and the student should acquire from it not only a very fair acquaintance with the main principles of chemistry, but also a knowledge of the apparatus and methods employed in elementary work in the laboratory. This section is followed by chapters in which the chemistry of the more important non-metals is systematically treated, and subsequently the metals are similarly discussed, and examples and questions in chemical calculations are added. The book contains a thoroughly sound scientific treatment of elementary inorganic chemistry, and can be recommended for the use of students other than those preparing for the London Matriculation.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 7, February 13, 1911.

Preparation of Isosparteïn.—Charles Moureu and Amand Valeur.—If the dichlorhydrate of α-methyl sparteïn is heated in a current of HCl, the salt isomerises into the chlorhydrate of the chloromethylate, which then decomposes into methyl chloride and the dichlorhydrate of isosparteïn. The yield is 90 per cent of the theoretical yield. Isosparteïn in contact with methyl iodide in boiling methylic solution fixes one molecule giving $C_{15}H_{26}N_2.CH_3I$. This product is a mixture of two distinct iodomethylates in which the CH_3I is fixed by the same nitrogen atom, and which therefore bear the same relation to one another as the α- and α'-iodomethylates of sparteïn.

Two New Methods of Synthesising Nitriles.—M. Grignard.—When cyanogen chloride acts on a mixed organo-magnesium compound the following reaction occurs: $-RMgX + ClCN = MgXCl + RCN$, and by this method various nitriles can be obtained. Other halogen derivatives of cyanogen do not react similarly. Nitriles can also be synthesised by allowing an organo-magnesium compound to drop into a cold ethereal solution of cyanogen, $RMgX + CN{-}CN = RCN + NCMgX$.

No. 8, February 20, 1911.

Uranyl Nitrate and its Ethereal Solution.—Paul Lebeau.—Uranyl nitrate as obtained by crystallisation from an aqueous solution at the ordinary temperature is a hydrate with six molecules of water. It dissolves in ether with evolution of heat and elimination of water. By cooling the solution and drying the crystals obtained in a current of air at the ordinary temperature the hydrate with three molecules of water is prepared. It is noteworthy that this hydrate retains its water of hydration even in presence of a strong dehydrating agent like dried calcium nitrate or metaphosphoric acid.

New Method of Determining Sulphuric Acid and Sulphates.—V. Auger and M. Gabillon.—The determination of sulphuric acid or sulphates may be effected by reducing them with hydriodic acid and determining the sulphuretted hydrogen formed by means of an iodine solution. It is best to prepare the HI in presence of the sulphate by mixing phosphoric and pyrophosphoric acids and potassium iodide; as the reaction $H_2SO_4 + 8HI = H_2S + 4H_2O + 8I$ sets free a large amount of iodine it is best to add phosphorous acid, which acts as follows: $-PO_3H_3 + 2I + H_2O = PO_4H_3 + 2IH$. The sulphuretted hydrogen is absorbed in a solution of zinc acetate, and then titrated with iodine in the usual way.

Condensation of Halogen Derivatives with $\beta\beta$-Dimethylglycidic Ether.—G. Darzens.—$\beta\beta$-Dimethylglycidic ether can be made to condense with methyl iodide in presence of a copper zinc couple, giving α-oxy-α-methylisovaleric ether. This reaction is general, and by it acids of formula—

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH{-}\underset{\displaystyle R}{\overset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}}{-}CO_2H,$$

and by dehydration the unsaturated acids $(CH_3)_2{-}CH{-}CHR{-}CO_2H$ can be prepared. By the action of sulphuric acid ketones of the type $(CH_3)_2{-}CH{-}CO{-}R$ can be obtained.

Action of α-Alkoxyl Acid Chlorides on Mixed Organo-metallic Derivatives of Zinc.—E. E. Blaise and L. Picard.—α-Bromocaproic ether reacts with sodium ethylate, giving α-ethoxycaproic ether. The corresponding acid is transformed by thionyl chloride into the acid chloride $CH_3 - (CH_2)_3{-}CH(O{-}C_2H_3)COCl$. This gives ethoxy-3-heptane with zinc ethyl iodide. By this process a secondary alcohol $R{-}CHOH{-}R'$ is obtained from a primary alcohol $R{-}CH_2OH$. The same method can be used for the preparation of the ether oxides of α-acid alcohols with a tertiary alcoholic function.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xliii., No. 18, 1910.

Behaviour of Acetic Acid Anhydride at High Temperatures.—Eug. Bamberger.—When strongly heated acetic acid anhydride yields very small quantities of acetone and still smaller quantities of acetyl acetone. The latter is probably a product of the acetylation of acetone.

Triaryl-methyls. — Wilhelm Schlenk and Anna Herzenstein.—The remarkable power of dissociation which is characteristic of "colourless triphenylmethyl" is analogous in principle to that exhibited by pentaphenylethane, though it differs from it in degree. The assumption that colourless triphenylmethyl is normal hexaphenylethane seems to be proved to be incorrect. The action of triarylchlormethanes on the corresponding triarylmethanes under the action of sunlight occasionally gives the corresponding hexarylethanes.

Vol. xliv., No. 2, 1911.

Constitution of Copper Acetylide.—Johannes Scheiber and Hans Reckleben.—Copper acetylide exists in the form of a hydrate, $C_2Cu_2H_2O$, and an anhydrous compound, C_2Cu_2. The acetylide is closely related to acetylene in constitution, for it is decomposed almost quantitatively into acetylene by the feeblest reagents, and the formula $CH{:}C.Cu.Cu.OH$ for the hydrate agrees well with all the experimental facts. There is no evidence of the isomerisation of the hydrate to form aldehydic compounds. The formula for the carbide suggested by Nef, $Cu_2C{:}C{\cdot\cdot}{\cdot\cdot}$, explains all the properties of the substance.

Salts of Pertitanic Acid with Organic Bases.—Eduard Kurowski and L. Nissenmann.—By the use of 30 per cent perhydrol the authors have obtained salts of pertitanic acid with methylamine, ethylamine, propylamine, dimethylamine, diethylamine, and dipropylamine. The salts are characterised by the large amount of active oxygen they contain, which suggests that either H_2O_2 of crystallisation is present in them, or else that the organic bases in them exist in the form of the corresponding peroxides. Sometimes the amount of active oxygen is so great that probably both explanations are correct. The

salts are light yellow or yellowish green. They are very unstable, and decompose rapidly at the ordinary temperature. They are very soluble in water, giving green solutions, and with dilute sulphuric acid they give H_2O_2. The ethylamine salt is the most stable of the primary amine compounds, and the methylamine the least. The secondary amine salts are much less stable than those of the primary amine, and tertiary amine salts have not been prepared.

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Bulletin de la Société Chimique de France.
Vol. ix.—x., No. 4, 1911.

Utilisation of a Magnetic Field to Determine Constitution.—P. Pascal.—In saturated fatty compounds of normal structure oxygen when bound to any two atoms whatever is always diamagnetic. In general it is magnetic when bound to a polyvalent element. When it is doubly bound to an atom of carbon already linked to a second atom of oxygen the first is diamagnetic. When an oxygen group contains an atom of tertiary carbon the rise of molecular diamagnetism is $-13{\cdot}5 \cdot 10^{-7}$, and the influence of external carbons is a periodic function of their distance from the oxygenated group. These results can be extended to the aromatic compounds.

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Atti della Reale Accademia dei Lincei.
Vol. xx., No. 2, 1911.

New Compounds of Hydrated Metallic Salts with Hexamethylene Tetramine. G. A. Barbieri and F. Calzolari.—The authors have previously described a series of compounds formed by the combination of metallic salts with hexamethylene tetramine, the general formula being $M''X_2.10H_2O.2C_6H_4N_{12}$, in which M'' represents magnesium, manganese, cobalt, or nickel, and X is chlorine, bromine, or iodine. By the action of the sulphocyanides, nitrates, and perchlorates of the same metals and ferrous sulphocyanide in concentrated aqueous solution on the concentrated solution of hexamethylene tetramine they have obtained crystalline salts of the following compositions:—

$M''(SCN)_2.4H_2O.2C_6H_4N_{12}$; M'' = Mn, Fe, Co, Ni.
$M''(SCN)_2.4H_2O.C_6H_4N_{12}$; M'' = Fe, Co, Ni.
$M''(NO_3)_2.10H_2O.2C_6H_4N_{12}$; M'' = Mg, Mn, Co, Ni.
$M''(ClO_4)_2.8H_2O.2C_6H_4N_{12}$; M'' = Mg, Mn, Co, Ni.

Direct Synthesis of Glycerides.—I. Bellucci and R. Manzetti.—By using the stochiometric quantities of oleic acid and glycerin, and gradually raising the temperature to 160—260°, the authors have demonstrated the possibility of obtaining in a short time almost the theoretical amount of glyceride.

MISCELLANEOUS.

Electrochemical Industry in Norway.—At a meeting of the Faraday Society, to be held on Tuesday, May 2nd next, Mr. A. Scott-Hansen, the well-known Norwegian Engineer, will deliver a lantern lecture on "Hydro-electric Plant in Norway and their Application to Electrochemical Industries." On the same evening a paper is down for reading by Mr. Verdon Cutts, of Sheffield, on "Electro-metallurgy in the Steel Foundry." The Society meets at the Institution of Engineers, Victoria Embankment, W.C., and the Secretary, Mr. F. S. Spiers, 82, Victoria Street, S.W., will be glad to send cards of admission to anyone interested desirous of attending the meeting.

Royal Institution.—On Tuesday next, April 25th, at 3 o'clock, Mr. J. E. C. Bodley begins a course of three lectures at the Royal Institution on (1) "Cardinal Manning," (2) "The Decay of Idealism in France and of Tradition in England," (3) "The Institute of France." On Thursday, April 27th, Prof. R. W. Wood, of the Johns Hopkins University, will begin a course of three lectures on "The Optical Properties of Metallic Vapours," these being the Tyndall Lectures, and on Saturday, April 29th, Prof. Selwyn Image delivers a lecture on "John Ruskin; or, The Seer and Art," to be followed on the two succeeding Saturdays by lectures on "William Morris" and "Walter Pater." The Friday evening Discourse on April 28th will be delivered by Prof. W. H. Flinders Petrie on "The Revolutions of Civilisation"; on May 5th by Prof. M. O. Forster on "New Organic Compounds of Nitrogen," and on May 12th by Prof. William Stirling on "Biology and the Cinematograph."

Free Places at the Imperial College of Science and Technology, 1911.—The London County Council has recently decided to make a maintenance grant of £8000 to the Imperial College of Science and Technology, South Kensington, S.W. In return for this grant it secures the privilege of nominating twenty-five students for one year's free instruction at the Imperial College. These places are to be filled as from October, 1911. The instruction will be of an advanced nature, and therefore only advanced students who are qualified to enter on the fourth year of the course should apply. There is no restriction as to income, but intending candidates must be ordinarily resident in the administrative County of London, and must be students at an institution aided, maintained, or approved by the Council, for this purpose, who have attended regularly courses of instruction for at least two sessions. The free studentships do not entitle the holders to any maintenance grants, but cover all ordinary tuition fees. No examination will be adopted for the final selection of the students from the applications received. The free studentships will be awarded on consideration of the past records of the candidates, the recommendations of their teachers, the course of study they intend to follow, and generally upon their fitness for advanced study in science applied to industry. It is quite possible that, in special cases, the free places may be extended to two or more years. Application forms (T. 2/268) can be obtained from the Education Officer, London County Council, Victoria Embankment, London, W.C., and must be returned not later than Saturday, May 27th, 1911.—R. Blair, Education Officer, L.C.C. Education Offices, Victoria Embankment, W.C.

NOTES AND QUERIES.

"*" Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Chemically prepared Colourless Papers.—I should be glad if someone will inform me where I can obtain chemically prepared colourless papers which change colour when the atmosphere becomes wet. There is one paper which turns to green, another to blue, and another to yellow.—Glazed.

MEETINGS FOR THE WEEK.

Tuesday 25th.—Royal Institution, 3. "Cardinal Manning," by J. E. C. Bodley.
Wednesday, 26th.—Royal Society of Arts, 8. "Production and Identification of Imitation and Artificial Gems," by Noel Heaton, B.Sc.
Thursday, 27th.—Royal Institution, 3. (The Tyndall Lecture). "The Optical Properties of Metallic Vapours," by Prof. R. W. Wood, LL.D.
— Royal Society of Arts, 4.30. "The Trend of Mineral Development in India," by Sir Thomas H. Holland, K.C.I.E., D.Sc., F.R.S.,
Friday 28th.—Royal Institution, 9. "The Revolutions of Civilisation," by Prof. W. M. Flinders Petrie, D.C.L., F.R.S., &c.
— Physical Society, 5. "High-tension Electrostatic Wattmeters," by E. Wilson. "Previous Magnetic History as Affected by Temperature, by E. Wilson and L. C. Budd "Behaviour of Incandescent Lime Cathodes," by R. S. Willows and T. Picton. "Formation of Dust Striations by an Electric Spark," by S. Marsh and W. H. Nottage.
Saturday, 29th.—Royal Institution, 3. "John Ruskin; or the Seer and Art," by Prof. Selwyn Image, M.A.

THE CHEMICAL NEWS.

VOL. CIII., No. 2683.

ON THE "HUGHES' REACTION" OF POTASSIUM IODIDE ON PAPER, AND ITS BEARING ON THE QUESTION OF ACIDITY IN PAPER.

By JAMES STRACHAN.

Introduction.

THE question of acidity in paper is essentially the question of the permanence of the latter, and the importance of this question may be realised best by the scientist when he considers the vast extent to which paper is used in the recording of his researches in the Transactions of Scientific Societies. Paper containing free mineral acid in its fibres is doomed to decay from the moment of its manufacture, the rate of decomposition depending upon two factors—(1) the amount of acid present, and (2) the power of the fibre to resist oxidation. The latter factor varies with the nature of the fibre, whether normal cellulose or oxy-cellulose. In the chemical examination of paper for acidity water-extracts are prepared from weighed samples, and these extracts are titrated with N 10 alkali, using—(A) congo-red as indicator, and (B) litmus as indicator. A is taken as "free acid," and B is taken as "combined acid" in the form of alum, an excess of which is generally used in the manufacture of paper.

Mr. E. Hughes, in a contribution on the subject of "Water as a Catalyst" (*Phil. Mag.*, [5], xxxv., p. 531), has incidentally given us, as the result of this present research will demonstrate, a new and delicate test for acidity in paper.

"Hughes' Reaction."

Hughes observed that paper, moistened with a solution of potassium iodide and exposed to light, assumed a brownish violet tinge. This colour was most intense with highly-glazed note-paper. He attributed the reaction to the liberation of iodine by free chlorine in the paper, and considered it from the point of view of water as a catalytic agent in promoting chemical change. This reaction attracted the attention of the well-known paper chemist Mr. Clayton Beadle, who studied it from another point of view, viz., iodide of potassium as an indicator of free chlorine or acid in paper ("Chapters on Paper-making," vol. i., p. 98).

Beadle's Work.

Beadle pointed out that highly-glazed note-paper of all papers is the least likely to contain free acid, and from a large experience of such papers dismissed Hughes' explanation as exceedingly improbable. Considering the reaction theoretically Beadle suggested the following possible causes :—

(1) Liberation of iodine from iodate in the potassium iodide by alum in the paper and subsequent staining of starch in the paper by iodine. He pointed out, however, that the colour produced by immersing paper containing starch in a dilute solution of iodine is an intense blue, and that this colour is rapidly discharged by exposure to sunlight.

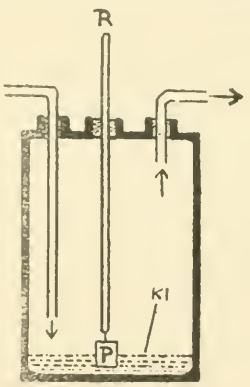
(2) Liberation of iodine from the potassium iodide by the action of atmospheric ozone and hydrogen peroxide.

After a discussion of the probabilities of the two theories suggested, Beadle finally comes to the conclusion, that the action of atmospheric ozone and hydrogen peroxide is the only satisfactory explanation of the staining n the Hughes' reaction. He also recalls the fact that atmospheric nitric acid is known to discolour starch-iodide paper. In view of the fact that many chemists regard the presence of ozone and hydrogen peroxide as normal constituents of the atmosphere, a doubtful circumstance, this conclusion appeared to the present writer as most unsatisfactory. Under ordinary conditions the amount of ozone and hydrogen peroxide in the atmosphere is so minute that it could not possibly produce the rapid results found in the Hughes' reaction. It is only under exceptional conditions, such as the discharge of atmospheric electricity and the rapid evaporation over large surfaces of water, that these compounds are formed in quantities.

The experiments and results recorded in this paper prove conclusively that ozone and hydrogen peroxide have nothing whatever to do with the staining, but that the latter is due entirely to chemical action taking place in the materials of the paper itself.

Action of various Gases on the "Hughes' Reaction."

In order to examine the action of various gases upon the "Hughes' reaction," a three necked bottle was arranged as in the sketch. The gas was introduced through one of the side-necks and made its exit by the other. The sample of paper P was introduced by the centre-neck and was fixed to the end of a glass rod R with platinum wire. The rod was free to slide up and down through the



paraffined cork of the centre-neck, thus providing a ready means for immersing the sample in the solution of potassium iodide, which latter was poured into the bottom of the bottle. Pure potassium iodide was used and the paper was one which gave an intense "Hughes' reaction" under ordinary conditions. The following gases were tried in this apparatus :—

1. *Air.*—It was found on passing air through the bottle that the ordinary reaction occurred. It was observed that the coloration was only slight, although distinct, on the immersed sample, but rapidly became intense when withdrawn from the solution. The colour was violet-brown.

2. *Air, previously Heated to a High Temperature by passing it through a Red-hot Combustion-tube, to destroy Ozone or Hydrogen Peroxide.*—The result was the same as in the case of air, but the reaction was a little more rapid.

3. *Air freed from Acid Vapours by passing it through a Caustic-soda Scrubber.*—Result : identical with ordinary air.

4. *Air containing Hydrochloric Acid Gas.*—Result : action more rapid and more intense.

5. *Air containing Chlorine Gas.*—Result : as with hydrochloric acid, but more intense.

6. *Air containing Ozone.*—Result : action very rapid and intense, but more of a blue tinge in the colour.

7. *Air containing Ammonia.*—Result : no coloration produced.

8. *Pure Hydrogen.*—Result: colour reaction exactly as with air.

The conclusions arrived at from these experiments were as follows:—

1. The chemical action of the atmosphere in "Hughes' reaction" is nil; its only function is drying or evaporation of the water.

2. The reaction is intensified by ozone, chlorine, and hydrochloric acid, suggesting that the real cause is the presence of an acid substance in the paper.

3. Iodine is liberated in the reaction and the coloration is bleached by ammonia.

It was further observed during these experiments:—

1. That the reaction takes place in the dark. The function of sunlight in the "Hughes' reaction" is thus probably the simple one of hastening evaporation.

2. That when the paper, coloured violet-brown by the reaction, is perfectly dried and then immersed in distilled water, the colour changes immediately to the characteristic bright blue of "starch iodide." This indicates that a further chemical action takes place on drying and immersion in water.

Microscopical and Chemical Examination of Samples of Paper.

Over two hundred samples of papers, including all classes of drawing, writing, and printing papers, were subjected to a systematic microscopical and chemical examination, including an application of the "Hughes' reaction." It was found that:—

1. The majority (about 90 per cent) of the papers did not contain any "free acid," yet many of these exhibited the characteristic coloration with the "Hughes' reaction."

2. All the papers which showed the characteristic coloration contained free (undecomposed) sulphate of alumina, and the intensity of the colour was directly proportional to the amount of alum present.

3. All the papers which showed the characteristic coloration also contained starch, the violet tinge of the coloration varying with variation of the amount of starch present.

4. Papers containing free sulphate of alumina and no starch gave a coloration varying from yellow to pale brown according to the amount of alum present.

5. No coloration was produced with unsized papers of any kind; for example, a type-writing (copy) paper composed of pure esparto grass cellulose was not discoloured by potassium iodide. This paper, of course, contained no alum.

6. The coloration was least in the case of tub-sized rag papers (in which only a very small proportion of alum is used to prevent the decomposition of the animal sizing) and most in the case of hard resin-sized papers composed of wood and esparto celluloses and containing an excess of alum (used to obtain the maximum effect of the resin-sizing).

7. The most intense effect was obtained with highly-glazed notepaper composed of pure esparto cellulose, containing excess of alum and 5—7 per cent of starch.

These results at once suggested that the cause of the decomposition of the potassium iodide in the "Hughes' reaction" is alum or sulphate of alumina.

Action of Potassium Iodide upon Cellulose.

In order to determine whether cellulose has any action in the decomposition of potassium iodide, samples of pure cotton cellulose and pure wood cellulose were prepared and moistened with the potassium iodide solution (20 per cent). The solution was allowed to dry on the cellulose in an acid-free atmosphere at 20° C. No discoloration was observed. The samples were then heated for thirty minutes at each of the following temperatures, viz.:—25° C., 80° C., and 100° C. At 80° C. an exceedingly faint yellow tinge was observed, which became more distinct at 100°. The conclusion arrived at from these experiments was that at ordinary temperatures, such as those at which the "Hughes' reaction" takes place, potassium iodide is not decomposed by cellulose, but that at higher temperatures a slight amount of decomposition or dissociation takes place.

Action of Potassium Iodide upon Starch.

Similar experiments were conducted with pure potato, maize, and rice starches, the varieties commonly used in paper-making. The results were identical with those arrived at with cellulose, except that the discoloration was not observed until the starch and potassium iodide were heated to 100° C. Starch does not, therefore, decompose or cause dissociation of potassium iodide at ordinary temperatures.

Action of Alum upon Potassium Iodide.

With the object of finding out the action of sulphate of aluminium upon iodide of potassium, 20 per cent solutions of these substances were prepared. The potassium iodide was pure, and the alum was free from "free sulphuric acid." A few drops of each solution were mixed on a sheet of glass, and dried at 20° C., 80° C., and 100° C. For the sake of comparison a duplicate series of experiments were carried out, using a few drops of 20 per cent solution of hydrochloric acid in place of the alum. The following colour reactions were observed:—

Dried at—	1. $H_2O + Al_2O_3.(SO_3)_3 + KI$.	2. $H_2O + HCl + KI$.
20° C.	Nil.	Pale brown.
80° C.	Faint yellow.	Dark brown.
100° C.	Pale brown.	Very dark brown.

The solutions when dried at 20° C. (in 1) were not decomposed. Upon examination of the residue under the microscope the characteristic cubes of crystalline KI were seen surrounded by spherical aggregates of $Al_2O_3.(SO_3)_3.Aq$. It was further observed that when dilute solutions of pure alum and pure potassium iodide are boiled no coloration is produced, but when saturated solutions of the same salts are boiled decomposition takes place with liberation of iodine and characteristic yellow colour. Further, when saturated solutions of the two salts are heated for a prolonged time, or evaporated down, a dark brown solid residue is obtained on cooling. This solid contained alumina, aluminium sulphate, potassium iodide, potassium sulphate, iodine, and a small amount of aluminium iodide.

The conclusions arrived at from these experiments were:—

1. That sulphate of aluminium and iodide of potash do not react with each other in the presence of water at ordinary temperatures.

2. That dilute solutions of these salts do not react at 100° C.

3. That strong solutions of these salts react at 100° C. with liberation of iodine.

4. That at higher temperatures than 100° C. these salts react with each other, a certain amount of double decomposition taking place, involving the liberation of iodine, which combines with potassium iodide and is also absorbed by alumina.

Action of Alum upon Potassium Iodide in Presence of Cellulose and Starch.

Similar experiments were then conducted with alum and potassium iodide in the presence of pure cellulose and pure starch. As before, for comparison, duplicate experiments were carried out, hydrochloric acid in place of alum. The results were as follows:—

Dried at—	$C_6H_{10}O_5 + H_2O + KI + Al_2O_3.(SO_3)_3$.	$C_6H_{10}O_5 + H_2O + KI + HCl$.
	1. *In the presence of Cellulose.*	
20° C.	Pale yellow.	Bright yellow.
80° C.	Bright yellow.	Brown.
100° C.	Dark brown.	Dark brown.
	2. *In presence of Starch.*	
20° C.	Pale yellow.	Violet-brown.
80° C.	Bright yellow.	Dark brown.
100° C.	Yellow with brown edges.	Dark brown.

From these experiments it was concluded:—

1. That the reaction between potassium iodide and aluminium sulphate takes place much more rapidly, and at lower temperatures in the pores of cellulose and starch.

2. That in paper containing cellulose, starch, and alum this reaction takes place on the application of a solution of potassium iodide.

Explanation of "Hughes' Reaction."

From the experiments already described it is quite clear that "Hughes' reaction" is caused by the mutual decomposition of alum and iodide of potash in the pores of the paper. It is therefore a delicate test for acidity due to alum in paper.

The cause of the reaction being most intense with "highly-glazed notepaper" is a simple one. The average specimen of such notepaper upon the market is a hard-sized pure Esparto grass paper, containing excess of alum. This smooth paper is highly calendered. Esparto grass is chosen for this class of paper because it stands calendering well. A large percentage of starch is added to give a smooth finish to the paper. Esparto fibre, too, of all fibres commonly used, has the property to a high degree of absorbing alum into its pores. A highly-glazed tub-sized notepaper composed of cotton and linen, and containing no starch, does not show the reaction.

The most probable chemical explanation of the reaction is as follows:—

1. The alum in paper exists in a partly dissociated state in the pores of the cellulose. This is due to the powerful affinity of cellulose for metallic bases, such as Fe_2O_3 and Al_2O_3.

2. When the solution of KI is applied to the paper, it enters the pores of the cellulose and the starch coating the cellulose. The $Al_2O_3.(SO_3)_3$ and the KI are then in solution in the pores of the paper. Under ordinary conditions they would not react visibly, but the molecular attraction of the cellulose, and starch also in all probability, for Al_2O_3 disturbs the balance. This takes place most rapidly in concentrated solutions. Therefore as the water evaporates the reaction proceeds, and is at a maximum when the moisture is almost completely evaporated. Al_2O_3 is absorbed by the cellulose, and iodine is liberated. The violet-brown coloration is due to iodine in the presence of saturated solutions of KI and $Al_2O_3.(SO_3)_3$, as may be proved by dissolving iodine in such a solution and applying it to a mixture of pure cellulose and starch.

3. When the reaction is at its maximum there is so little water present that part of iodine remains where formed in the pores of the cellulose. When the violet-brown spot is dried and pure water applied, the water dissolves some of the KI (which is in excess), and the solution of KI dissolves the iodine, which immediately flies to the starch, staining it the characteristic bright blue colour.

This appears to be a complete and satisfactory explanation of the reaction, but we have yet to consider its bearing upon acidity in paper.

The Bearing of "Hughes' Reaction" upon the Acidity of Paper.

It is a well known fact that "free acid" in paper, whether derived from over-bleaching (HCl) or from impure alum (H_2SO_4), has a deteriorating effect upon the cellulose, producing oxidation of the latter and consequent disintegration. It has also been observed that papers containing an excess of uncombined or undecomposed alum suffer a similar oxidation. This fact is usually attributed to the Al_2O_3 present, which is supposed to act as a carrier of oxygen in much the same fashion as Fe_2O_3 and CuO, which cause "tendering" or oxidation of cellulose by a process of alternate oxidation and reduction (*vide* Beadle's "Chapters on Paper-making," vol. i., p. 97). In the case of iron oxide, the oxidation of organic matter containing it, by alternation of the ferrous and ferric states, is well known, and in the case of copper oxide (in paper) it has been shown by the present writer that a similar alternation of the cuprous and cupric states prevails ("On Dendritic Growths of Copper Oxide in Paper," *Journ. Royal Microscopical Society*, 1908, pp. 544—550).

In the case of alumina, however, we have no evidence of a lower state of oxidation, and in the action of free alum in paper the conclusion is borne in upon us that it is the acid radical and not the basic which attacks the cellulose. If we take a piece of paper, immerse it in a solution of aluminium sulphate, dry it, and then expose it to a temperature of 110° C. for twenty-four hours, it is found to be more or less "tendered" or oxidised. In some cases it becomes quite brittle. Normal celluloses, such as cotton and linen resist this action much better than oxy-celluloses, such as those derived from Esparto grass and wood. Some organic salts of aluminium have a similar but more feeble action on cellulose. In the latter case it is well to remember the fact that many organic acids have a "tendering" effect upon cellulose, quite as certain as, although inferior in degree to, mineral acids. In short, we must regard the "combined acid" of free alum in certain papers as negative to their permanence. Slower in its action than "free acid,' it is not less certain in its ultimate effects. In the manufacture of paper for permanent records the sizing should be as nearly neutral as possible.

Practical Application of "Hughes' Reaction" in Testing Paper.

In conclusion, it remains to describe the practical application of the "Hughes' reaction" as a test for detecting the presence of uncombined alum in paper.

After examination for "free acid" by applying a solution of congo-red, a small square of the paper is placed upon a glazed tile, and a single drop of 20 per cent pure iodide of potash solution applied to the surface of the paper. It is then covered with a watch-glass, and left in an acid- and ammonia-free atmosphere for an hour. Paper containing uncombined alum and starch is stained a reddish or violet-brown, and paper containing the former and not the latter is stained a bright yellow, the degree of colour in each case being proportional to the amount of alum present. In the case of paper which does not contain starch, the violet-brown reaction may be produced by using a solution of potassium iodide in which starch has been dissolved. A paper which gives an intense reaction on the application of this test must be regarded with suspicion as to its value for purposes of permanent records, and should be subjected to rigorous physical and chemical tests, including exposure, for at least twelve hours, to the atmosphere at a temperature of 100—110° C. in an air- or steam-oven.

Chemical Laboratory,
Ballyclare, Co. Antrim,
March, 1911.

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.*

FIRST PAPER.—THE ANALYSIS OF NEODYMIUM CHLORIDE.

By GREGORY PAUL BAXTER and HAROLD C. CHAPIN.

(Continued from p. 187).

The Separation of Neodymia from other Rare Earths.

IT is a well-known fact that when a salt of a mixture of rare earths is subjected to fractional crystallisation, the less soluble salts tend to concentrate at the less soluble end of each series of fractions, and the more soluble salts at the opposite end of the series. In most cases it is less difficult to free an earth very thoroughly from more soluble impurities than it is to eliminate impurities which tend to concentrate in the crystals. An obvious although not

* *Journal o the American Chemical Society*, xxxiii., No. 1.

generally recognised way out of the difficulty is to crystallise the substance in such different forms that impurities which tend to concentrate in the crystals in one case, concentrate in the mother-liquors in another, continuing the crystallisation in any one form until impurities which accumulate in the mother-liquors have been eliminated as completely as possible.

In the present instance the material was crystallised first as double ammonium nitrate from dilute nitric acid, then as nitrate from concentrated nitric acid. According to Auer von Welsbach (*Sitzungsber. Akad. Wiss. Wien*, 1903, cxii., 1043), in crystallisation as double ammonium nitrates the bases separate in the order, lanthanum, cerium, praseodymium, neodymium, samarium, terbium, and yttrium earths, while, according to Demarçay (*Comptes Rendus*, 1896, cxxii., 728; 1900, cxxx., 1021), in the crystallisation of the nitrates from nitric acid the solubility first decreases with increasing atomic weight through gadolinium, 157·2, and then increases. In the crystallisation as double ammonium nitrates samarium and the more soluble earths were eliminated, while in the crystallisation of the nitrates from nitric acid the solubility of the first four of the above nitrates is reversed and the lanthanum, cerium, and praseodymium were removed in the mother-liquors.

Three and one-half kilogrms. of neodymium ammonium nitrate, very kindly furnished by Dr. H. S. Miner, of the Welsbach Light Company, served as a starting-point in the preparation of pure material. The history of this material is somewhat uncertain, but, as nearly as can be determined, is as follows:—Swedish cerite was decomposed with acid, and the rare earths were precipitated as oxalates, from which the oxides were obtained by ignition. These oxides were then treated with nitric acid and the insoluble basic ceric salt was produced by heating. The lanthanum, praseodymium, neodymium, samarium, yttrium, &c., were obtained in solution. After the addition of ammonium nitrate the material had received, probably, about 150 to 250 crystallisations. Our treatment showed it to contain considerable lanthanum, cerium, and praseodymium, and a small amount of samarium. Probably traces of other rare earths were present, but no evidence of their existence was found even in the extreme fractions of the purified material.

In the further purification to which we subjected the double neodymium ammonium nitrate the usual method of fractional crystallisation was followed: — The whole material (1) was crystallised and the crystals (2) were separated from the mother-liquor (3). The crystals were dissolved and again crystallised, the crystals becoming (4) and the mother-liquor (5). The mother-liquor (3) was evaporated to crystallisation, and the crystals were combined with (5), while the mother-liquor formed (6), and so on indefinitely. After the first few series of crystallisations the number of fractions in each series was maintained nearly constant between twenty and twenty-five, and the different fractions were not allowed to vary much in size. As a rule the solutions were allowed to become supersaturated by cooling without crystallisation, then they were seeded with tiny crystals of the purest neodymium salt available, and allowed to stand undisturbed over night in order that by the formation of large crystals the removal of mother-liquor might be facilitated. On account of the extra labour and time involved, centrifugal drainage of the crystals is of little advantage where the composition of crystals and mother-liquor differs as slightly as in the present case, and therefore was not employed. When the end fractions become small they were either temporarily removed and added to similar fractions subsequently obtained, or, if it could be plainly seen by the difference in colour that they contained considerable impurity, they were ejected.

When eighty-six series of crystallisations had been completed, spectrograms were made of the absorption spectra of selected fractions in the last series, which contained fractions 1287 to 1309. These photographs were taken on Cramer's trichromatic plates with a spectrograph employing glass lenses and prisms and covered the range λ 650—λ 380. The spectra indicated the presence of samarium in only a few of the more soluble fractions, 1306 to 1309. Praseodymium could be detected in all the fractions, although only traces were visible in the more soluble fractions.

In order to throw more light upon the progress of the purification, approximate atomic weight determinations by the "permanganate" method were carried out with portions of fractions 1290, 1299, 1303, and 1305. The oxalate was precipitated by adding a dilute solution of an excess of pure oxalic acid, and the precipitate was thoroughly washed, collected, and dried at 120—130°. After very complete mixing of the highly crystalline material by grinding in an agate mortar, weighed portions of the oxalate were converted to oxide by ignition in platinum crucibles. Other portions, weighed out at the same time, were dissolved in dilute sulphuric acid and titrated with a standard solution of potassium permanganate. From the ratio $M_2O_3 : 3C_2O_4$ the atomic weight was calculated.

Fractions 1299 to 1305 were evidently very nearly identical and probably nearly pure, while fraction 1290 apparently contained about 10 per cent of praseodymium, cerium, and lanthanum.

At this point fraction 1302, which seemed on the whole to be the purest in this series, was set aside for more careful examination and analysis. Fractions 1303 to 1309 also, which contained the bulk of the remaining samarium and yttrium earths, were separated from the others, and the fractionation was continued as before.

No further accumulation of samarium could be detected, after seventeen more series of crystallisations had been completed, in a spectrographic examination of the more soluble fractions of the one hundred and third series. Nevertheless the two most soluble fractions, 1615 and 1616, were rejected, and the next, 1614, was removed for subsequent analysis.

The sharpness with which the samarium is removed from the neodymium by the crystallisation of the double ammonium nitrate is striking in comparison with the difficulty in eliminating the last traces of praseodymium in the same way. After the removal of only eight fractions, 1302 to 1309, the last of which was comparatively rich in samarium, seventeen series of crystallisations failed to reveal any residual samarium. On the other hand, when the fractions 1303 to 1309 were subjected to further fractional crystallisation by themselves, the least soluble fraction of the fourteenth series was found to contain about one-half per cent of praseodymium, estimated spectrographically as described later. By the same method fraction 1302, which contained more praseodymium than any one of the seven crystallised, was found to contain only 0·2 per cent of this impurity. Demarçay (*Comptes Rendus*, 1900, cxxx., 1021) and Feit and Przibylla (*loc. cit.*, p. 207) have emphasised the fact that neodymium and samarium may be separated with equal facility by crystallisation as double magnesium nitrates.

At this point it seemed reasonably certain that practically all the more soluble rare earth impurities had been eliminated, while evidence of praseodymium could still be seen in the absorption spectra of all the fractions. For the removal of the praseodymium and at the same time cerium and lanthanum, if present, crystallisation of the nitrates from concentrated nitric acid was next undertaken, since in this process these elements accumulate in the mother-liquors (Demarçay, *loc. cit.*).

The ammonium nitrate was removed from the different fractions by evaporation and ignition, concentrated nitric acid was added, and the crystallisation was carried through sixty-seven series. The same numbering was continued, except that the order of the one hundred and third series was reversed to give the less soluble fractions the lower numbers as before, 1613 becoming 1613*a* and 1596 becoming

Fraction.		Proportion of Nd_2O_3.	Proportion of C_3O_4.	Atomic weight.
1290		0·5334	0·4193	—
		0·5334	0·4194	—
		—	0·4195	—
	Average ..	0·5433	0·4194	143·9
1299		0·5454	0·4274	—
		0·5452	0·4281	—
		—	0·4278	—
		—	0·4279	—
	Average ..	0·5453	0·4278	144·3
1303		0·5412	0·4258	—
		0·5412	0·4258	—
	Average ..	0·5412	0·4258	143·8
		0·5391	0·4217	—
		0·5390	0·4228	—
		—	0·4218	—
		—	0·4221	—
	Average ..	0·5390	0·4221	144·6
		0·5379	0·4212	—
		—	0·4212	—
	Average ..	0·5379	0·4212	144·6
	Average of second and third values ..			144·6
1305		0·5447	0·4269	—
		0·5448	0·4272	—
		—	0·4272	—
		—	0·4269	—
	Average ..	0·5448	0·4271	144·4
		0·5414	0·4236	—
		—	0·4242	—
	Average ..	0·5414	0·4239	144·6
			Average ..	144·5

1630. During these sixty-seven series no fractions were rejected at the less soluble end, although the extreme mother-liquor was frequently rejected. Thus any nitrate less soluble than neodymium nitrate would concentrate in the extreme crystal fraction of the last series.

The fractions of the last series, 2923 to 2945, were then converted to oxide by precipitation as oxalate from acid solution and ignition of the oxalate. The different fractions of oxide were all of the same lilac-blue colour. We could detect no difference in the colour of the oxides of fractions found to be essentially free from praseodymium and those containing several tenths of a per cent of this impurity.

The final fractions were next subjected to careful comparative spectrographic examination, great pains being taken to have the conditions of experimentation the same for all the fractions. One grm. of every third fraction was dissolved in nitric acid, and, after the excess of acid had been evaporated, the solutions were diluted to the same volume, about 5 cc. Photographs of the absorption spectra were made, the solutions being contained in test-tubes of the same diameter, and various lengths of exposure being employed. The samarium band λ 401 was faintly visible in fraction 2923 only. This is not surprising, however, since, as has been stated before, no fractions had been removed from the less soluble end of the series in the course of all the sixty-seven series of crystallisations from concentrated nitric acid. Praseodymium could not be detected in fractions 2923 to 2932, but its strongest absorption band, λ 444, appeared with regularly increasing intensity in fractions 2935 to 2944.

In order to find out how much praseodymium can be detected in this way, and at the same time to estimate the proportion of praseodymium in the latter fractions, spectrograms were made, on one plate, and with the same exposure, of the spectra of most of the solutions previously examined, and also of others similarly prepared from fractions 1302 and 1614, which had been removed at earlier stages of the fractionation. To a solution of fraction 2926, in which no praseodymium could be detected in the first photograph, 0·1 per cent of praseodymium oxide was added in solution, and the original concentration was restored by evaporation. The absorption spectrum of this specimen was photographed on the same plate as above, and again after the praseodymium content had been increased to 0·2, 0·5, and 1·0 per cent respectively. In the negative the first addition of 0·1 per cent made a distinct impression. From this it was concluded that fractions 2923 to 2932 contained less than that proportion of praseodymium. This assumption can scarcely be objected to on the ground that a considerable amount of praseodymium in fraction 2926 might have been brought within the limits of detection by means of a relatively small increment, because the intensity of the praseodymium band appeared to be proportional to the amounts of praseodymium added to the original solution.

Since these standards and the other solutions differed little except in praseodymium content, those giving praseodymium spectra of equal intensity could be safely assumed to contain the same percentage of this impurity. The results of the comparison of the different spectrograms are as follows:—

Fraction	2935	2938	2941	2944	1302	1614
Per cent of Pr ..	0·05	0·1	0·2	0·5	0·2	0·15

Since a proportion of one-tenth of a per cent of praseodymium lowers the atomic weight of neodymium by only four one-thousandth of a unit, the purer fractions were obviously as pure as it is worth while to make them. None of them in all probability were entirely free from praseodymium. In fact, visual spectroscopic examination of both fraction 2929 and 2931 with very strong absorption showed them to contain perceptible amounts of this impurity.

It is reasonable to suppose that cerium and lanthanum nitrates, which are more soluble in concentrated nitric acid than praseodymium nitrate, were removed from the neodymium even more completely than praseodymium. Evidence upon this point is more difficult to secure than in the case of praseodymium, on account of the lack of absorption bands of cerium and lanthanum in the visible spectrum. The following test for cerium was carried out with fraction 2944, which contained 0·5 per cent of praseodymium. The hydroxide was precipitated by the addition of an excess of sodium hydroxide, and, after washing by decantation, it was treated with saturated chlorine water for some time. A small quantity of undissolved hydroxide was filtered off and dissolved in nitric acid. To the nearly neutral solution a sufficient amount of a solution of calcium hypochlorite was added to produce a slight permanent precipitate. This precipitate was pink with no tinge o yellow. The same solution, after the addition of a trace of cerium and testing with hypochlorite as before, yielded a precipitate distinctly coloured with the characteristic yellow of ceric hydroxide. Fraction 2944 was evidently nearly, if not entirely, free from cerium and the less oluble fractions of the series must have been purer still.

(To be continued).

A PHYSICO-CHEMICAL STUDY OF MERCURY SODIUM ALLOYS OR SODIUM AMALGAMS.*

By ERNEST VANSTONE (B.Sc., Wales), 1851 Exhibition Research Scholar, University College of South Wales and Monmouthshire.

(Continued from p. 185).

The Determination of the Specific Volumes of Mercury-sodium Alloys.

1. *Liquid Alloys.*—The high melting-points of the metals have hitherto prevented many density determinations in the liquid state. The alkali metals, however, have low melting-points, and are therefore suitable for this purpose. Density determinations of sodium amalgams were undertaken for two reasons (1) to find whether any evidence could be obtained of the existence of metallic compounds in the liquid state; (2) if such were the case, to find whether any relation could be traced between volume and valency.

The determination of the density of liquid sodium appeared at first to be a task of great difficulty, owing to the adhesion of the metal to glass and the rapidity with which it oxidises.

All attempts to fill dilatometers by pouring in the sodium were unsuccessful; it was found, however, that the sodium could be readily drawn up into pipettes, and this was the method adopted. A pipette as in Fig. 4 was made, and its capacity determined by weighing with mercury. The pure sodium was obtained as described in the first part of the paper, and kept under paraffin, thus entirely preventing oxidation.

The method of filling the pipette can be seen from Fig. 5.

The tube A containing the sodium was heated in a vapour jacket, B.

The pipette was placed within the tube A, and was connected to a carbon dioxide apparatus and a small hand suction-pump as shown. When the temperature was steady the carbon dioxide was turned off, and the metal drawn up into the pipette by pulling out the piston of the hand-pump. When the metal had reached the mark on the pipette the stopcock was turned off, the pipette removed, cleaned, and weighed. The amalgams were made by adding mercury to the fused sodium in A. Sodium has been heated to 100° C., 184° C., and 237° C., and the mercury then added, amalgamation taking place quietly. The densities of the amalgams were determined in the same manner.

A quantity of sodium sufficient for two or three determinations at the same concentration was weighed out in the tube A. The tube was then cleaned, an alloy of different concentration made, and its specific volume determined.

A new pipette was made and calibrated for each determination, a correction being applied for the expansion of the glass. Determinations were made at temperatures close to the melting-points of these alloys. It was thought that by so doing greater changes in volume would be observed. The specific volumes of those alloys melting below 237° C. have been determined. Alloys of concentrations varying from 100 per cent to 66 per cent sodium were determined at 110° C., using toluene in the vapour jacket.

Alloys from 66 per cent to 59 per cent and 15 to 0 per cent were determined at 184° C., using aniline in the vapour jacket.

A few concentrations varying from 58 to 47 per cent have been determined at 237° C., using quinoline in the vapour jacket. The results are given in Table V. In the first column are given the concentrations expressed in atoms of sodium per 100 of mixture.

Column 2 contains the observed specific volumes.

Column 3 contains the specific volumes calculated from the formula—

$$V = \frac{w_1 v_1 + w_2 v_2}{w_1 + w_2},$$

* A Paper read before the Faraday Society, March 14, 1911.

TABLE V.—*Specific Volumes at* 110° C.

Concentration. Sodium per cent.	Specific volumes. Observed.	Mean.	Calculated.	Contraction.	Percentage contraction.
100	1·0829 1·0786 1·0770 1·0801 1·0778 1·0800	1·0794	—	—	—
96·956	0·85216 0·85273	0·85245	0·86404	0·01159	1·3414
95·634	0·77738 0·77923 0·77923	0·77863	0·79432	0·01569	1·9753
92·588	0·63673 0·63692 0·63462	0·63609	0·66774	0·03165	4·7399
90·124	0·55944 0·55980	0·55962	0·58997	0·03035	5·1443
87·217	0·48543 0·48123 0·48291	0·48319	0·51733	0·03414	6·5993
85·863	0·45355 0·45390	0·45372	0·48873	0·03501	7·1635
84·500	0·42553 0·42527	0·42540	0·46273	0·03733	8·0674
83·477	0·40559 0·40563	0·40561	0·44479	0·03918	8·8086
82·861	0·39499 0·39538	0·39518	0·43458	0·03940	9·0662
81·966	0·38145 0·38151	0·38148	0·42047	0·03899	9·2729
80·262	0·35490 0·35490	0·35490	0·39567	0·04077	10·304
77·605	0·32018 0·32026	0·32022	0·36183	0·04161	11·500
75·286	0·29389 0·29378	0·29383	0·33619	0·04236	12·600
73·293	0·27465 0·27520	0·27492	0·31656	0·04154	13·154
70·722	0·25068 0·25050	0·25059	0·29394	0·04335	14·748
69·102	0·23838 0·23834	0·23836	0·28102	0·04266	15·180
68·736	0·23594 0·23610	0·23602	0·27826	0·04244	15·180
66·627	0·22254		0·26305	0·04051	15·400
66·064	0·21764		0·25924	0·04160	16·047
	Specific Volumes at 184° C.				
Sodium	1·1043 1·1036	1·1040	—	—	—
66·627	0·22702		0·26859	0·04157	15·477
63·992	0·21016		0·25108	0·04092	16·260
62·968	0·20347 0·20360	0·20353	0·24477	0·04124	16·849
61·483	0·19625		0·23604	0·03979	16·858
59·254	0·18453		0·22386	0·03933	17·569
12·048	0·08488		0·09204	0·00716	7·779
8·157	0·08220		0·08647	0·00426	4·926
4·7907	0·07971		0·08197	0·00226	2·7642
2·2855	0·07772		0·07879	0·00107	1·3631
	Specific Volumes at 237° C.				
58·234	0·18165		0·22212	0·04047	18·220
57·586	0·17993		0·21881	0·03886	17·760
54·710	0·16853		0·20506	0·03653	17·814
50·924	0·15396		0·18892	0·03495	18·500
50·040	0·15317		0·18541	0·03224	17·388
49·380	0·14861		0·18288	0·03427	18·739
48·249	0·14644		0·17865	0·03221	18·030
19·985	0·09451		0·10611	0·01160	10·931
19·087	0·09274		0·10455	0·01161	11·105
17·273	0·09139		0·10139	0·01000	9·862
100	1·1247		—	—	—

where—

w_1 = number of grms. of sodium,
w_2 = number of grms. of mercury,
v_1 = specific volume of sodium,
v_2 = specific volume of mercury.

Column 4 contains the difference between the observed and calculated specific volumes. The values in this column may be termed specific contractions.

Column 5 contains the percentage contractions.

In Fig. 6 the specific volumes determined at 110° C. have been plotted against concentrations. The curve obtained is smooth, whereas the corresponding portion of the freezing-point diagram possesses two discontinuities at concentrations of 85 and 74 per cent respectively.

Although the study of the freezing-points has led to the construction of a highly complex thermal diagram showing marked discontinuities, it does not necessarily follow that all other physical properties should show similar discontinuities. The transition from the eutectic at a concentration of 85 per cent to the compound Na_3Hg at 75 per cent is a gradual process; a very small proportion of the compound being first formed with corresponding diminution in the proportion of the eutectic mixture, hence we may expect gradual changes in the specific volume of alloys in this neighbourhood, and also throughout the whole series of alloys.

It is difficult to decide which of the two following conclusions is the correct one.

1. Are the compounds Na_3Hg and Na_3Hg_2 entirely dissociated in the liquid state at 110° C.?

2. Is the volume change too small to indicate the existence of compounds?

It will be shown later that the specific volumes of the solid alloys also lie on a smooth curve, and as compounds have been proved to exist in the solid state, the second conclusion appears to be the correct one.

Additional evidence in support of this is obtained by plotting percentage contractions against concentrations. Fig. 7 shows the results at 110° C. The diagram consists of two straight lines intersecting at a concentration of 74 per cent. The gradual increase in the percentage contraction is obvious. It must be pointed out, however, that the error of experiment is multiplied in calculating percentage contractions, since the difference between the observed and calculated values of the specific volume multiplied by 100 is involved, or percentage contraction $C = \left(\frac{v_c - v_b}{v_c}\right) 100$, where v_c = calculated specific volume and v_b = observed specific volume. The deviations from the straight line at 110° C., are, however, obviously greater than experimental error. No abnormal contraction is observed at 85 per cent, where the eutectic begins to change into the compound Na_3Hg.

Fig. 6.

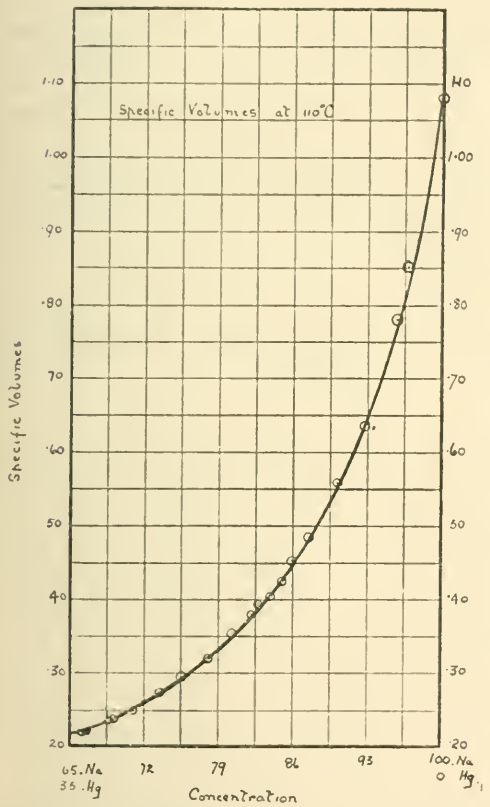


Fig 7.

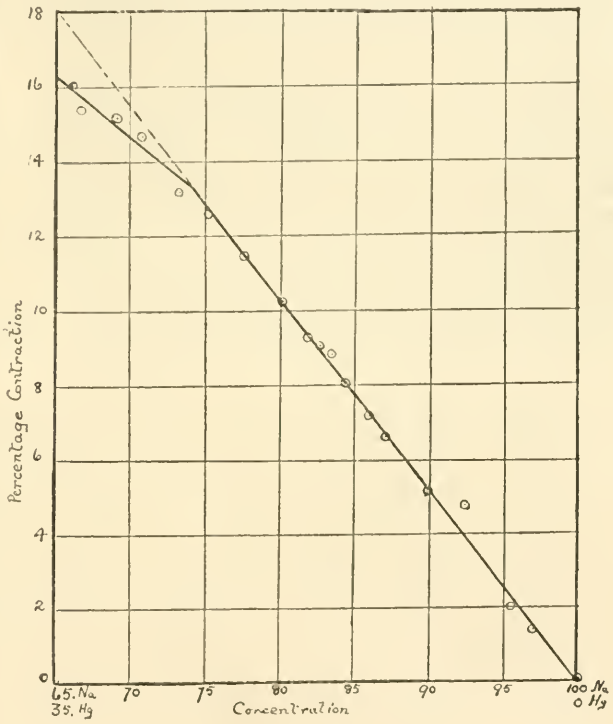


Fig. 8 is the diagram of specific volumes for temperatures 184° C. and 237° C. Again, a smooth curve has been obtained. Those points determined at 184° C., are indicated by means of a circle. The percentage contractions at 184° C. again lie on a straight line with the exception of that at 63 per cent (Fig. 9). At this concentration the compound Na_3Hg_2 begins to change into NaHg.

The contractions at 237° C. do not lie on a regular line, and peaks occur at 51 and 49 per cent. Although Fig. 9 does not furnish trustworthy evidence as to the existence of compounds in liquid mercury-sodium alloys at 237° C.

owing to the greater errors of experiment, yet it serves to show the maximum of contraction in this neighbourhood. This is of interest in connection with the corresponding small branch in the thermal diagram.

Quite recently Bornemann and Muller (*Metallurgie*, vii., 1910), in a research on the electrical conductivities of iquid mercury-sodium alloys at high temperatures, obtained strong evidence of the existence of the compound $NaHg_2$ in the liquid state in a highly undissociated condition; no evidence of the existence of other compounds was obtained.

Alloys having the composition indicated by $NaHg_2$ melt at 353° C. Consequently (on account of the obviously great difficulties), the specific volumes in this neighbourhood have not been determined.

Before leaving the question of liquid alloys, it must be pointed out how the present work throws light on the work of other investigators.

Ramsay (*Trans. Chem. Soc.*, 1889, p. 521), from observations of the lowering of the vapour pressure of mercury by dissolved sodium, found that the molecular weight of sodium when dissolved in mercury falls with increasing proportion, and suggested that this might be due to the formation of a stable alloy of sodium and mercury, which acts as a solvent.

This explanation is undoubtedly the correct one, as amalgams having the concentrations of those under investigation consisted of mixtures of eutectic and the compound $NaHg_4$. Guntz and Ferée (*loc. cit.*) succeeded in isolating this compound. In the course of the work I have found when mercury is added to an alloy of the composition denoted by $NaHg_2$, which melts at 353° C., this alloy dissolves at a much lower temperature.

Heycock and Neville (*Trans. Chem. Soc.*, 1892, lxi., 890), in discussing the causes of change in the atomic depression of the freezing-point when various metals were dissolved in tin, state:—"No increase in the volume of the solvent is assumed, so the osmotic pressure is by Boyle's law directly

Fig. 8.

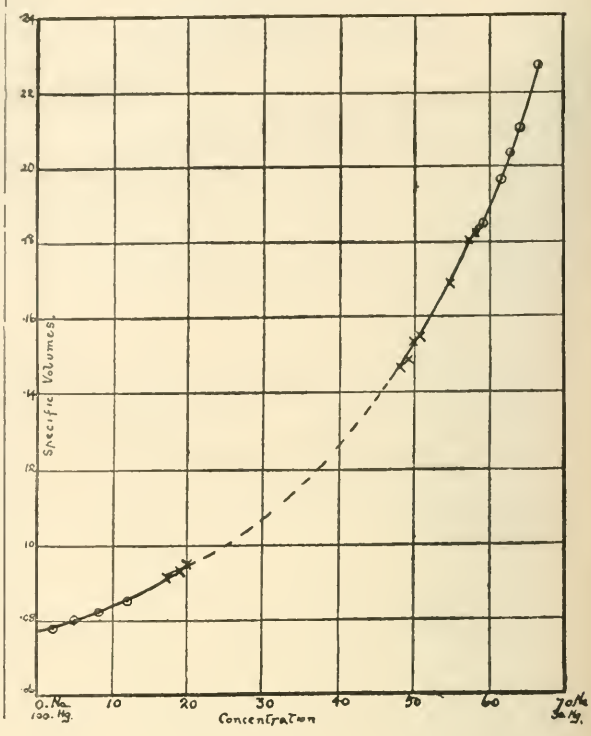
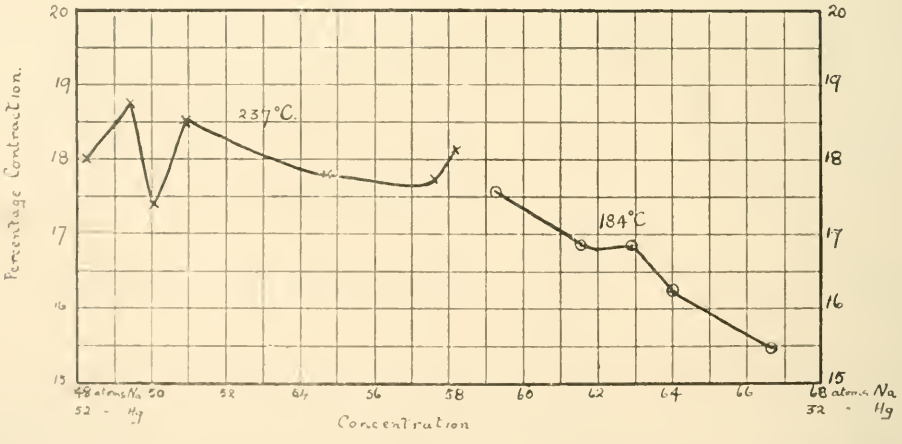


Fig 9.



proportional to the amount of the dissolved body. This is an improbable assumption. The determination of the densities of liquid alloys would probably throw light on this question."

It has already been stated that large contractions occur, and that contraction increases with concentration up to a certain point, and then diminishes. Contraction would lead to an increased osmotic pressure, and hence to a higher atomic lowering of the freezing-point than that calculated from the van't Hoff formula. This is precisely what occurs. The theoretical atomic fall is approximately 3° C. Heycock and Neville found that for mercury in sodium the atomic depression was 4·5° C.

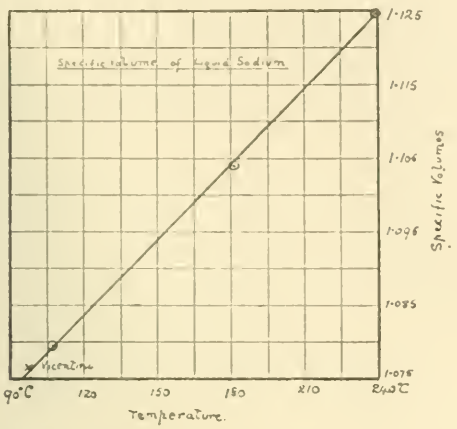
The Specific Volume of Liquid Sodium.

In the course of the work the specific volumes of liquid sodium have been determined at three different temperatures, namely, 110° C., 184° C., and 237° C. The values obtained are given below:—

Temp. (°C.).	Specific volume.	Atomic volume.
110	1·0794	24·826
184	1·1040	25·392
237	1·1247	25·868

The specific volumes have been plotted against temperature in Fig. 10; the three points are seen to lie on a

straight line, so that the relation between volume and temperature from 110° C. to 237° C. is linear.



Vicentini and Omodei obtained the value 1·0767 at 98° C. (Landolt-Bornstein "Tabellen," p. 105*b*).

Ramsay obtained 1·349 as the specific volume at the boiling-point (*Trans. Chem. Soc.*, 1881, xxxix., 49).

(To be continued).

ALLOYS OF NICKEL AND COBALT WITH CHROMIUM.

By ELWOOD HAYNES.

The metals nickel and cobalt have always possessed a peculiar interest for the chemist. Like nearly all of the more recently discovered metals, their compounds were known before the metals themselves were discovered. Indeed, it has been known for centuries that certain substances were capable of giving a blue colour to glass, and there is but little doubt that this peculiar power was due to some crude compound of cobalt.

About two centuries ago, the ores of cobalt and nickel were encountered in the mining of copper. It was at first supposed that they were ores of the latter metal, but the miners, after vainly striving to smelt the ore, and failing to obtain any copper from it, designated it as "kupfernick," and from this expression the world "nickel" originated.

Attempts were also made to smelt the ores of cobalt, but as no useful metal resulted, they decided that the goblin, or "kobold," supposed to inhabit the mines, had placed a ban upon the ore, and thus rendered it incapable of producing valuable metal. From this designation, by the German miners, the name "cobalt" was derived.

It was not until 1751 that Cronsted published the results of an investigation which he had made upon an ore obtained from the mines of Helsingland. This ore yielded a brittle metal, and as it occurred most abundantly in "kupfernickel," he suggested for it the name of nickel.

A few years later, in 1776, it was discovered that nickel was evidently one of the constituents of a Chinese alloy, known as "packfong."

The use of nickel in German silver began about the year 1823. It was not, however, until 1857 that Messrs. Deville and Debray, the celebrated French chemists and metallurgists, prepared pure nickel by heating its oxalate in a lime crucible. From the pure metal thus obtained wires were made, which showed a tensile strength superior to that of wrought iron. The wires also showed considerable toughness, and when polished presented a bright, silvery appearance, and retained their lustre for an indefinite period, under all ordinary atmospheric conditions.

A few years later the art of electroplating nickel was discovered and has since received a very wide application. Tons of the double sulphate of nickel ammonium are used for this purpose every year.

Besides this latter important application of the metal, it is now used in large quantities for the manufacture of nickel steel, which has become a common substance in the making of naval guns, projectiles, armour plate, and high-class automobiles.

The history of cobalt is similar to that of nickel, excepting that the compounds of cobalt were used in the arts, instead of the metal itself. In fact, but little was known of the metal until 1857, when Deville produced the pure metal in practically the same manner that nickel was prepared. It was found that cobalt was even stronger than nickel, possessing a tensile strength of about 65,000 pounds per square inch. Indeed, up to that time, it was the strongest pure metal discovered, and it still holds this position with the possible exception of tantalum.

About the year 1895 I made a number of tentative experiments relating to the production of alloys of nickel with iron, chromium, and other metals. The fusions were made in small graphite crucibles, which were heated in a blast-furnace of the Fletcher type, operated by natural gas. I had at that time the advantage of natural gas at a pressure of forty pounds or more per square inch. With a suitably arranged furnace of this character, temperatures ranging up to the fusing point of the most refractory Missouri fire-clay were readily obtained. I succeeded in obtaining by this means alloys of nickel and chromium, which contained, however, a considerable amount of carbon and silicon. A small quantity of aluminium was sometimes added to the alloy in order to improve its quality. By this means I obtained an alloy of chromium, nickel, and aluminium, which was hard and brittle, but possessed fairly good colour and lustre. From this alloy a knife blade was formed, which showed fair cutting qualities and considerable resistance to atmospheric conditions. It was readily soluble in nitric acid, and after long exposure to the atmosphere of a chemical laboratory it became tarnished, showing a greenish coating on its surface.

Later, I attempted to produce alloys of nickel and chromium with titanium, by means of an electric furnace, made from blocks of quicklime. This proved unsatisfactory, but I continued experimenting with the gas furnace, and, finally, succeeded in producing an alloy of nickel and chromium entirely free from carbon by heating the pure mixed oxides of the two metals with powdered aluminium, in a crucible lined with pure oxide of aluminium. The reaction was so violent that most of the metal was thrown from the crucible. A few small pellets were saved and these showed great malleability, flattening readily under the hammer, without cracking. The alloy possessed a fine colour, and when polished exhibited a beautiful lustre. Larger pellets were soon obtained, and it was found that when the chromium content much exceeded ten per cent that the alloy showed remarkable resistance to chemical reagents, particularly to nitric acid.

At about the same time I reduced a mixture of the sesquioxides of cobalt and chromium with powdered aluminium, and thus obtained minute pellets of an alloy of cobalt and chromium. The little particles thus produced were not much larger than pinheads. They were found to be remarkably hard and could scarcely be scratched by a file. A few of them were ground off on one side by means of carborundum and showed a brilliant lustre. It occurred to me that the metal might become serviceable for cutting instruments.

A short time after the above experiments were made I was called actively into the automobile business, and thus compelled to abandon further experiments along this line for some time.

In 1905 I repeated some of the former experiments, with

a view to utilising the alloys of cobalt and nickel with chromium for ignition points, in connection with gas engines. I was soon able to produce both the alloys of nickel and cobalt in considerable quantity. I ascertained that the nickel-chromium alloy could be worked cold, while the cobalt-chromium alloy must be worked hot in order to obtain any degree of satisfaction.

The first pellets of the cobalt-chromium alloy, weighing from fifteen to thirty grms., were obtained by heating mixtures of aluminium with the oxides of cobalt and chromium in crucibles lines with the oxide of aluminium. Some of these pellets were heated to redness and flattened out under the hammer, and while this could be done without cracking the alloy, the metal was found to be very hard even at red heat.

I soon found that it was impracticable to reduce the alloy in this manner in large quantities. I accordingly purchased a considerable amount of pure cobalt and pure chromium, and had a mixture of nearly equal parts of these metals fused in an electric furnace, the metals being placed in a carbon crucible lined with pure magnesia. The alloy was cast into a small bar, about one-fourth of an inch square, and five or six inches long. This alloy exhibited most of the characteristics of that obtained by reduction with aluminium, but it could not be drawn to any extent under the hammer without cracking. Whether this was due to the high percentage of chromium, or to slight impurities in the metals employed, I am as yet unable to say.

In order to determine what the effect of alloying the cobalt with smaller percentage of chromium would be, I again had recourse to the gas furnace, and succeeded in melting a mixture containing 75 per cent cobalt and 25 per cent chromium in a crucible made of a very refractory material, which I compounded for the purpose. Much to my satisfaction, I succeeded in melting this alloy to a perfect fluid and poured it into an ingot mould, which gave me a bar of metal about one-half an inch square and five or six inches in length. The metal proved to be very sonorous and elastic, and if some care were used it could be hammered out into a rough strip.

After a considerable amount of experimenting with various purifying agents I finally succeeded in producing a very tough and malleable alloy, which could be hammered out into the thinnest sheet at a bright red heat without showing any sign of cracking. A razor blade was made from a bar of this alloy, and while it did not prove equal to the best steel for this purpose, it has been used hundreds of times for shaving purposes, and after a year and a half shows practically no signs of wear, though, of course, it has been necessary to strop it frequently in order to keep it in good condition. The bar was made about two years ago, and I am sure that I have since produced metal that would be much more satisfactory for the purpose.

A test of tensile strength and elastic limit of this material was made, with results as follows:—Elastic limit 79,000 lbs.; tensile strength 96,000 lbs.; elongation, 3 per cent. It will be seen from the above that both the elastic limit and tensile strength of this material are superior to those of untreated steel, resembling more nearly those of good nickel steel. The elongation is quite low, but this is to be expected on account of the great hardness of the alloy, which is equal to that of mild tempered tool steel. A test was also made of the modulus of elasticity of this material, which was found to be about equal to that of steel. This is a very significant fact, since heretofore it has not been possible, so far as I am aware, to form an alloy of non-ferrous metals which would show a modulus of elasticity comparable to that of iron and steel. And it is lack of this valuable property in various non-ferrous mixtures which renders them inferior to iron for many important purposes.

A pocket knife blade and several table knife blades were made from this material, and were found to be very satisfactory in every respect. One of these table knife blades has now been in use for more than two years in the kitchen, where it was used for all sorts of purposes, such as cutting bread, turning griddle cakes, peeling and paring vegetables, and for various other purposes such as are known only to the culinary art. After all this use and abuse, the knife shows not the slightest trace of tarnish, and has held its lustre so well that when exposed to the sun it shows a reflection which dazzles the eyes.

By mixing the alloys with small quantities of other substances its properties may be modified to a remarkable degree. By this means I have obtained alloys, or combinations, which, while very brittle, would readily scratch quartz crystal.

By reducing the quantity of chromium to some extent, and adding certain other materials, alloys which are practically proof against nitric acid can readily be obtained which are sufficiently soft and malleable to be worked cold, having a hardness not much greater than that of mild, untempered steel.

Between these two extremes a great variety of combinations can be made which are suitable for use for various purposes. For example, I have produced an alloy of sufficient hardness that when it is formed into a small bar, say one-half an each wide, one-fourth an inch thick, and three inches long, and one of the ends shaped for a cold chisel, a twenty-penny nail can be cut in two without marring the edge of the chisel in the slightest degree. I have formed another alloy into a small lathe tool, about one-fourth an inch square and three inches long, which showed cutting qualities comparable to high-speed tool steel. In fact, in some respects, especially under high speed and light cuts, it has stood the test for a long time, where high-speed steel failed almost instantly, on account of the intense heat generated. I wish it distinctly understood, however, that I do not recommend this material as yet for lathe tools, though it would have a high value for this purpose if it were not obliged to compete with alloy steels.

An alloy of 75 per cent cobalt and 25 per cent chromium, to which small quantities of other metals are added, is not only sufficiently hard for good edge tools, but is quite tough, and can be bent much beyond its elastic limit without cracking, resembling in this respect the alloy steels, but, generally speaking, it is much harder. A bar of the alloy, one-fourth nch square, can be bent at right angles without showing any signs of cracking.

Chemical Properties.

When the mixture of cobalt and chromium is heated to whiteness in a crucible, the cobalt first commences to fuse and immediately begins to combine with the chromium, and if the metals are mixed in the proportion of about three parts, by weight, of cobalt to one of chromium, a eutectic is formed seems to process a lower melting-point than either cobalt or chromium.

The colour of the alloy lies between that of steel and silver, and is especially pleasing in bright light. The alloy is also readily polished, but requires special treatment in order to develop its highest lustre.

The most remarkable property of this combination, however, is its resistance to corrosion. It is equalled in this repect only by gold and the metal of the platinum group. It is attacked slowly by dilute hydrochloric acid and somewhat vigorously by the strong acid, especially when heated. Momentary exposure, however, to either dilute or strong hydrochloric acid has practically no effect on the metal. Both strong and dilute sulphuric acid attack it very slowly when cold, and not very rapidly even when heated. Nitric acid is totally without action upon it, and a polished piece of the alloy may be boiled in that substance for hours without affecting the lustre of the metal in the slightest degree.

Solutions of the caustic alkalis are also totally without action upon it, even when boiled for hours. The alloy is likewise proof against all atmospheric influences, whether the air be moist or dry, and retains its brilliant lustre for

months, or even years, under severest conditions. Even sulphuretted hydrogen, when present in the atmosphere in large quantity, is totally without action upon it.

Its resistance to culinary operations has already been mentioned.

When the metal is heated in contact with the atmosphere it retains its colour up to a temperature approaching a dull red, or about 500°, when it shows a faint straw-colour, which deepens as the temperature rises, passing through bronze-yellow, purple, blue, and finally terminating in blue-black.

The alloy shows no scale, even when heated to bright orange, and the film of oxides does not seem to increase in thickness after prolonged heating.

It can readily be melted in an open crucible in a gas furnace with practically no oxidation, so long as a slightly reducing flame is maintained. This is all the more remarkable on account of its high melting-point, which seems to be about 1650° C. for the 25 per cent alloy. Indeed, the metal has been melted in this manner with a loss of less than one-half of 1 per cent.

Uses.

The uses for any substance may be limited in several particulars: first, by the limitations of its fitness; second, by the possibility of producing it in proper form; and third, by its cost. This material is particularly suitable for all kinds of small cutting instruments, since it takes an edge comparable to that of tempered steel. It is especially adaptable to the manufacture of pocket knifes, on account of the beauty of its colour and the brilliancy of its lustre, both of which remain permanent under all circumstances, thus giving the blades a particularly attractive appearance. Knives of this description may be used for cutting fruit without danger of marring their lustre in the slighest degrec.

Alloys in certain proportions will also doubtless find a wide use for surgical instruments, since they resist perfectly all sterilising solutions.

The alloy is perhaps better adapted for table cutlery than anything that has ever yet been produced. We all know too well that a silver-plated knife, for example, is ill adapted for cutting meat, and it cannot be sharpened without destroying the plating. Steel knives, on the other hand, while they cut well, require endless labour to keep them in presentable condition, and at best they are unsightly in appearancc.

The alloy is also of considerable interest to the chemist and physicist. It is admirably adapted for the manufacture of fine weights for balances, scrapers, spatulas, and other laboratory appliances. To the physicist, it furnishes a material which is at once hard, lustrous, and untarnishable, and hence well adapted for the manufacture of fine weights, measuring instruments, and various small tools.

The alloy is also particularly well adapted for the manuacture of standard weights and measures, such as the grm., kilogrm., metre, &c., and it is difficult to see in what respect it is inferior for this purpose to the expensive platinum-iridium alloy now in use.

The alloy could readily be made into laboratory vessels, cooking utensils, spoons, forks, &c., and it is limited in this respect only by its cost.

Cost.

Regarding the cost of production and manufacture, I am not at present prepared to make definite statements. I have succeeded, however, not only in obtaining the raw material at lower prices, but have also reduced the cost of production to a considerable degree, so that it is now possible to produce the alloys with as much despatch and precision as is possible in the production of common alloys.—*Journal of Industrial and Engineering Chemistry*, ii., No. 10.

CORRESPONDENCE.

THE CHEMICAL SIGNIFICANCE OF CRYSTAL STRUCTURE.

To the Editor of the Chemical News.

SIR,—In the January number of the *Central Magazine* (also in CHEMICAL NEWS, vol. ciii., p. 149 *et seq.*) there is an article on the above subject by Prof. Pope, F.R.S., in which reference is made to the homologous series of normal paraffins, and the following table is given, in which the molecular volumes at the respective melting-points of each substance are calculated by multiplying the valency volumes, W (or sum of the valencies of the molecule), by a constant, 2·970:—

	W.	Melting-point, *t*°.	Molecular volumes. Observed at *t*°.	Molecular volumes. Calculated as W × S.
$C_{11}H_{24}$	68	−26·5	201·4	201·96
$C_{12}H_{26}$	74	−12·0	219·9	219·78
$C_{13}H_{28}$	80	− 6·2	237·3	237·60
$C_{14}H_{30}$	86	+ 4·5	255·4	255·42
$C_{15}H_{32}$	92	+10·0	273·2	273·24
$C_{16}H_{34}$	98	+18·0	291·2	291·06
$C_{17}H_{36}$	104	+22·5	309·0	308·88
$C_{18}H_{38}$	110	+28·0	326·9	326·70
$C_{19}H_{40}$	116	+32·0	344·7	344·52
$C_{20}H_{42}$	122	+36·7	362·5	362·34
$C_{21}H_{44}$	128	+40·4	380·3	380·16
$C_{22}H_{46}$	134	+44·4	398·3	398·00
$C_{23}H_{48}$	140	+47·7	416·2	415·80
$C_{24}H_{50}$	146	+51·1	434·1	433·62
$C_{27}H_{56}$	164	+59·5	487·4	487·08
$C_{31}H_{64}$	188	+68·1	558·4	558·36
$C_{32}H_{66}$	194	+70·0	576·2	576·18
$C_{35}H_{72}$	212	+74·7	629·5	629·64

It would be a help to the student of the interesting theory put forward by Prof. Pope if he would explain how the constant 2·970 is obtained.

If we are at liberty to select any suitable number for a constant, the molecular volumes can be calculated from the molecular *weights* instead of from the aggregate valancies, and the constant 1·285 will serve the purpose.

In the fifth column of the above table W × S. there is a regular difference of 6 × 2·970 = 17·82; there is, however, an irregularity in the observed molecular volumes that deserves attention, and which is apparent if the differences are taken out, thus:—

	Melting-point, *t*°.	Molecular volumes observed at *t*°.	Differences in molecular volumes.	Differences in melting-points.
$C_{11}H_{24}$ ..	−26·5	201·4		
			18·5	14·5
$C_{12}H_{26}$ ..	−12·0	219·9		
			17·4	5·8
$C_{13}H_{28}$ ..	− 6·2	237·3		
			18·1	10·7
$C_{14}H_{30}$ ..	+ 4·5	255·4		
			17·8	5·5
$C_{15}H_{32}$ ..	+10·0	273·2		
			18·0	8·0
$C_{16}H_{34}$ ..	+18·0	291·2		
			17·8	4·5
$C_{17}H_{36}$ ..	+22·5	309·0		
			17·9	5·5
$C_{18}H_{38}$ ..	+28·0	326·9		
			17·8	4·0
$C_{19}H_{40}$ ..	+32·0	344·7		
			17·8	4·7
$C_{20}H_{42}$ ..	+36·7	362·5		

The differences in molecular volumes are evidently dependent upon the differences in melting-point where the alternating character of the variations in consecutive members of the series is most marked. These variations in melting-point are in accord with a well-known feature of carbon chains which is especially noticeable in the series of monobasic and dibasic acids, and may also be traced back in the lower members of the series of normal paraffins.

	Melting-point.	Difference.
C_9H_{20}	−51°	20·0
$C_{10}H_{22}$	−31°	4·5
$C_{11}H_{24}$	−26·5°	14·5
$C_{12}H_{26}$	−12°	
&c.	&c.	&c.

It seems reasonable to ask that any theory which appeals for support to the molecular volumes of a series of hydrocarbons should give evidence of its validity by producing results coincident with these important irregularities.—I am, &c.,

EDW. E. PRICE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other ise expressed

Bulletin de la Société Chimique de France.
Vol. ix.—x., No. 5, 1911.

Utilisation of Magnetic Field to Determine Constitution. - P. Pascal.—When an open chain contains an oxygen bound to two identical groups, or an oxycarbon group bound to two identical radicles, the effects of tertiary or quaternary carbons mutually destroy one another by symmetry. The author concludes his paper with a long list of compounds with their calculated and observed molecular susceptibilities.

Rate of Decomposition of Dissolved Dithionic Acid.—J. A. Muller.—In an acid medium sodium dithionate dissolved in water acts slowly on iodine according to the equation $Na_2S_2O_6 + I_2 + 2H_2O = 2NaHSO_4 + 2HI$. The velocity of the reaction is that of a mono-molecular reaction. Apparently the reaction is in reality the resultant of three successive reactions:—(1) The liberation of free dithionic acid, (2) the decomposition of the dithionic acid into sulphuric acid and sulphuric anhydride, (3) the action of iodine on the latter.

Catalysis in a Homogeneous System.—J. A. Muller.—The author has measured the effect of variations in temperature and concentration of hydrochloric acid on the magnitude of the quantity $K = \frac{1}{t} \log \frac{1}{1-x}$ in the reaction between sodium dithionate and iodine. He finds that this constant is greater the richer the mixture is in HCl, so that the latter acts as a positive catalyser of the decomposition. It is the acid itself which acts as catalyser and not its ions. The equation expressing the value of K as a function of the absolute temperature $T = 273 + D$ is $K = n(\alpha\gamma^T - 1)(b^T - 1)$ where $n = 4{\cdot}6 \times 10^{-22}$, $a = 1{\cdot}0023$, $b = 1{\cdot}1458$.

Determination of Bromine in presence of Chlorides and Iodides.—P. Clausmann.—By a modification of the methods of Déchan and Carnot, bromine can be very accurately determined in presence of chlorides or iodides. The solid mixture or the concentrated solution is treated with chromic acid and pure sulphuric acid, and heated on a bath for an hour. It is then cooled, and half the liquid is distilled over into a solution of potassium iodide, and the iodine set free is titrated with 1/100 N sodium hyposulphite. The bromine is easily calculated from the iodine. Even in presence of large quantities of chlorides three quarters of the liquid can be distilled over before chlorochromic acid is formed. If iodine is present it passes over with the bromine, and must be determined previously.

True Cyclic Acetylenic Hydrocarbons, Phenylbutine.—Emile André.—Phenylbutyline can be transformed nto phenylbutine by brominating in chloroform, evaporating *n vacuo*, and treating the dibrom-addition product with alcoholic potash. After boiling with a reflux condenser or an hour ether is added, the ethereal solution is dried, the ether is evaporated off, and the residue is fractionated *in vacuo*. Bromophenyl - butylene, $C_6H_5.CH_2.CH_2.CH = CHBr$, passes over between 123° and 125°. When its sodium derivative is decomposed by water containing a little hydrochloric acid, phenylbutine is obtained as a colourless liquid boiling at 189—191° under 758 mm.

Contardi's Polyphosphoric Ethers of Mannite, Quercite, Glucose, and Inosite.—P. Carré.—The author has repeated Contardi's experiments for the preparation of mannitohexaphosphoric acid and its barium salt, and also the corresponding salts of quercite and inosite and the barium salt, $C_6H_7(PO_4Ba)_7$, of the heptaphosphoric acid of glucose; by titration he has found that the phosphoric acid is present in them in the free state. Thus the compounds described by Contardi are in reality mixtures of phosphoric acid and the corresponding alcohols or their decomposition products with a small quantity of monobarytic phosphate.

MEETINGS FOR THE WEEK.

MONDAY, May 1st.—Royal Institution, 5. Annual Meeting.
—— Society of Chemical Industry, 8. "Testing of Creosote," by C. E. Sage. "Modification of Raschig's Theory of the Lead Chamber Process," by E. Divers.
—— Royal Society of Arts, 8. (Cantor Lecture). "Rock Crystal, its Structure and Uses," by Dr. A. E. H. Tutton.

TUESDAY, 2nd.—Royal Institution, 3. "The Decay of Idealism in France and of Tradition in England," by J. E. C. Bodley.
—— Faraday Society, 8. "Hydro-electric Plants in Norway, and their Application to Electrochemical Industry," by A. Scott-Hansen (Christiana). "Electro-metallurgy in the Steel Foundry," by V. Cutts. "Two Simple Forms of Gas-pressure Regulators," by E. Stansfield.

WEDNESDAY, 3rd.—Royal Society of Arts, 8. "Improvements in the Transport and Distribution of Goods in London," by A. W. Gattie.
—— Society of Public Analysts, 8. "Evaluation of certain Spices used in Medicine," by J. C. Umney and C. T. Bennett. "Absorption of Dissolved Oxygen by Sewage Effluents and the Royal Commission's Provisional Standard," by E. Halliwell. "Detection of Traces of Hydrogen Cyanide," by G. D. Lander and A. E. Walden. "Composition of 'Blaud's Pills'" and "The 'Pearl Coating' of Pills," by A. E. Parkes and J. D. Roberts. "Reaction for 'Caulophyllin,'" by J. F. H. Gilbard.

THURSDAY, 4th.—Royal Institution, 3. (The Tyndall Lecture). "The Optical Properties of Metallic Vapours," by Prof. R. W. Wood, LL.D.
—— Royal Society. "Some Phenomena of Regeneration in Sycon, with a Note on the Structure of its Collar-cells," by J. S. Huxley. "Cancerous Ancestry and the Incidence of Cancer in Mice," by J. A. Murray. "Motor Localisation in the Brain of the Gibbon correlated with a Histological Examination," by F. W. Mott, E. Schuster, and C. S. Sherrington. "Immunisation by means of Bacterial Endotoxins," by R. T. Hewlett.
—— Chemical, 8.30. "Constituents of Bryony Root," by F. B. Power and C. W. Moore "Action of Hydrogen Dioxide on Thiobenzanilide," by H. Leete and E. de B. Barnett. "Purification of Acetic Acid," by K. J. P. Orton, Miss G. M. Edwards, and H. King. "Detection and Estimation of Small Quantities of Acetic Anhydride in Acetic Acid," by Miss M. G. Edwards and K. J. P. Orton. "Tetramethylammonium Hyponitrite and its Decomposition under Heat," by P. C. Ray and H. K. Sen. "Reactivity of the Halogens in Organic Compounds—Part VI., Mechanism of Negative Catalysis, by G. Senter and A. W. Porter. "Second and Third Dissociation Constants of Orthophosphoric Acid," by E. B. R. Prideaux. "Experiments on Tautomerism—Part I., Tautomerism of the System X CHR—CR=CR—X showing the Identity of the α- and γ-positions in the Glutaconic Acid Molecule," by F. B. Thole and J. F. Thorpe.

FRIDAY 5th.—Royal Institution, 9. "New Organic Compounds of Nitrogen," by Prof M. O. Forster, F.R.S., &c.

SATURDAY, 6th.—Royal Institution, 3. "William Morris; or the Craftsman and Art," by Prof. Selwyn Image, M.A.

THE CHEMICAL NEWS.

Vol. CIII., No. 2684.

A MODIFICATION OF RASCHIG'S THEORY OF THE LEAD CHAMBER PROCESS.

By Dr. E. DIVERS, F.R.S.

Raschig's theory is that nitrous acid unites with sulphur dioxide, molecule with molecule, to form a substance unknown of the inferred composition $HNSO_4$, and that this interacts with a second molecule of nitrous acid to produce nitric oxide and a substance H_2NSO_5, also unknown, but perhaps to be identified with the colouring matter to be seen sometimes in the acid in the Gay-Lussac tower when there is faulty working. Finally, the H_2NSO_5 decomposes into sulphuric acid and more nitric oxide.

The author of this paper agrees with the principle of the theory, but cannot accept the suggestion that these two substances, called by Raschig nitroso- and nitrosi-sulphonic acids, are formed and take part in the production of sulphuric acid. Particularly, he contends that the existence of the latter of the two is chemically impossible to admit.

The intermediate substance must have the composition shown in the formula $H_2N_2SO_6$, because it is the sum both of $2HNO_2+SO_2$ and of $2NO+H_2SO_4$, these pairs being, one, the active substances, and the other the final products. He points out that nitrous acid (or its equivalent) must combine with the sulphur dioxide if it is to be active in changing the latter into sulphuric acid.

The intermediate substance he calls nitroxysulphuric acid, because of its close serial relationship to the acid of Pelouze's potassium nitroxysulphite. Nitroxysulphuric acid appears to be sulphonated nitroxous acid, this being the name given by the author to Thum's azohydroxyl or Angeli's nitrohydroxamic acid, $H_2N_2O_3$, an acid half way between hyponitrous and nitrous acids. The author's constitutional formulæ are—

Nitroxous acid, $HON\langle{}^{O}_{O}\rangle NH$;

Nitroxysulphuric acid, $HON\langle{}^{O}_{O}\rangle NSO_3H$;

Nitroxysulphurous acid, $HN\langle{}^{O}_{O}\rangle NSO_3H$.

The author shows that an explanation can now be given of the long-recognised peculiarity that the volume of atmospheric oxygen which must enter the lead chamber is, roughly measured, equal to that of the sulphur dioxide, and therefore twice as much as has seemed chemically necessary. The explanation rests upon Raschig's observations of the atmospheric oxidation of nitric oxide. The immediate product is of the composition N_2O_4, but differs, for a short time, from ordinary nitric peroxide in being nitrous peroxide, ONO·ONO, a substance which acts upon water as a nitrous compound, oxygen being liberated. Since SO_2 needs as much nitrous acid as that derived from 2NO, and 2NO combine with O_2 as nitrous peroxide, the process in the lead chamber is expressed by the equations:—

$$2NO+O_2=ONO\cdot ONO;$$
$$2N_2O_4+2H_2O=4HNO_2+O_2;$$
$$2HNO_2+SO_2=H_2N_2SO_6=2NO+H_2SO_4.$$

These equations show all the oxygen as used up, temporarily, by the nitric oxide, yet only to produce the peroxide of nitrous acid.

Since, outside the chamber, nitrous acid so steadily unites with two molecules of sulphur dioxide, it has been hitherto a difficulty to understand how, in the chambers where sulphur dioxide is present in large excess, nitrous acid should there combine with so much less sulphur dioxide. The reason is, according to the author, that the nitroxysulphuric acid, decomposing as fast as it is formed, produces the chamber mist, consisting of minute drops of sulphuric acid, surrounded each by an atmosphere of unmixed nitric oxide. The nitric oxide, diffusing into the chamber atmosphere of sulphur dioxide and oxygen, largely diluted with nitrogen, is in excess of the sulphur dioxide and oxygen that it meets, until it has all become nitroxysulphuric acid, which is itself unacted upon by the constituents of that atmosphere.

THE FRUIT OF *VIBURNUM LENTAGO*.

By C. E GILLETTE

Viburnum lentago is the largest and most important o three very similar species:—(1) *Viburnum lentago*, the swee viburnum, wild raisin, or sweet black-haw; (2) *Viburnum prunifolium*, the stag bush, or small black-haw; (3) *Viburnum rufotomentosum*, the southern black-haw.

The *Viburnum lentago* grows on a shrub or bush from 8 to 20 feet in height. The leaves, slender petioled, ovate rounded at the base, and acuminate at the apex, 2 to 4 inches in length; cyme, sessile, several rayed, 2 to 5 inches broad; drupes, oval, bluish black, wood hardy; fruit abundant.

It grows in rich wet soil along stream bottoms, as underbrush in forests and waste lands from Quebec and Manitoba South to Georgia, and from the Alleghanies West to Kansas. It flowers about May, and the fruit ripens the first of October. The fruit is sweet and edible, furnishing food for our autumn birds, and may even be used as a substitute for raisins.

The fruit for this analysis was gathered in a second growth timber between Mount Vernon and Lisbon, Iowa, early in October, 1909. They were unusually large and sweet, and were still plump and in fine condition. The average weight was found to be 0·3233 grm. On drying they lose nearly half their weight, but retain their natural shape and colour. They are dark blue or black with a bloom of light blue. Each resembles a Rugby football in shape, with a length of 1 cm. and a breadth of 9 cm. A black mushy pulp surrounds a hard brittle pit of a dirty brown colour without and a light yellow within. The pit is about 9 cm. in length, 7 cm. broad, and 2 cm. thick in the centre. Enclosed within the pit is a similarly shaped seed. Without it is reddish brown in colour, and within pure white.

The Sugars.

Two portions of the fruit of 100 grms. each were treated for the sugars. They were placed in 500 cc. flasks fitted with inverted condensers, and treated daily with successive portions of alcohol. The extract was at first a deep red or wine colour, but it gradually became lighter from day to day. It had a sweetish taste and odour, and was nearly neutral to litmus during the entire time of extraction. No gums nor resinous substances were found.

After forty days distilled water was substituted for alcohol. Ten days were required to remove the last traces of sugar. This extract was darker, and contained much more sediment, because the fruit became mushy under the water treatment.

The alcohol and water extracts were filtered to remove the sediment, and the sugar determined separately in each filtrate. Fehling's solution was used. One cc. of the alcoholic extract was evaporated to remove the alcohol, diluted to 50 cc. with water, and titrated with the Fehling's solution. One cc. of the water extract was treated in the same way. The residue and sediment from the two extractions were thoroughly dried and weighed. The results of the two determinations are as follows:—

	1.	2.
Alcoholic extract (per cent) ..	56	57
Water extract (per cent)	2·5	2·0
Total (per cent)	58·5	59
Weight of residue (grms.)	40	40

The sugar and residue together make 98·5 and 99 grms. respectively, which leaves 1 per cent and 1½ per cent unaccounted for.

After the amount of sugar had been determined the extracts were united and evaporated. Attempts were made to obtain crystals, but were unsuccessful. Other tests were then made to determine the nature of the sugars. The phenylhydrazine test, according to Sherman and Williams (*Journ. Am. Chem. Soc.*, xxviii., 629, May, 1906), showed fructose and a small quantity of dextrose to be present. Cobalt nitrate also indicated dextrose. Lime added to an ice-cold sugar solution indicated a small quantity of levulose. Tests for dextrine were unsatisfactory.

The Oils.

The dried residue from the two portions used in the sugar extraction was finely ground, placed in a 50 cc. flask fitted with an inverted condenser, and treated daily with successive portions of ether. The ether was removed from the oil by distillation. No chlorophyll was found to be present. The oil seemed to be pure, and was a beautiful light amber in colour. However, it was treated with bone-black to remove any possible contamination. The oil from 200 grms. of fruit weighed 8·5020 grms., equivalent to 4·25 per cent.

The oil was a clear light amber with a few globules of a dark red heavy oil. Owing to the small quantity of the red portion no attempt was made to determine it, but it was removed so as not to interfere with testing the main portion. The lighter had a consistency of sperm oil. The odour was characteristic, though a faint odour of the oil of hickory nuts was thought to be recognised also. The taste was sweetish and mildly penetrating.

An attempt was made to solidify the oil, but it only became slightly thicker at −24°. At intervals for a month after extraction the specific gravity was determined with the following results:—

Time after extraction, in days	1	10	25	30
Specific gravity	0·8654	0·8800	0·8971	0·9039
Temperature	15°	16°	18°	15°

This showed that the oil was either oxidising or drying. A portion of it was transferred to a beaker, heated to about 70°, and allowed to cool. In a few minutes a thin film was found forming on the surface, becoming quite thick within an hour. The oil was then heated to boiling, and a thin coat applied to a polished white ash surface. The oil dried to a light shiny surface, and the wood retained its natural white colour. The oil became thicker and darker after heating.

About a grm. of the oil was saponified by Koetstorfer's method. It was heated twelve hours, and gave a value of 218, which would place it near cocoanut oil.

The unsaponifiable portion was extracted with ether from the soapy solution and evaporated to constant weight. The amount obtained was 0·2547 grm., or nearly one-fourth of the weight of oil taken. When this amount was subtracted from the weight of oil used for the saponification the value was found to be 166, but nothing in the literature seemed to correspond to this number. It had a rancid odour like old oil of hickory nuts, and was reddish amber in colour. It would not all crystallise, although a few minute crystals were obtained from it.

After extracting the unsaponifiable oil with ether the saponification product was acidified with sulphuric acid and heated to about 50°, the fatty acids freed by saponification collecting upon the surface. They were removed, washed, placed in a flask, and distilled water added. The flask was then fitted to an inverted condenser and boiled for several hours. They were then removed to a crucible and dried to constant weight, which was found to be 0·62 grm. They had an odour like lard. There appeared to be a yellowish brown layer above with a clear layer beneath. The darker acid solidified at −12° to −14°, and was probably oxidised impure oleic acid. The solidifying temperature of the clear acid was about 0°.

A light soluble acid, solidifying at 25—30°, was separated from the saponification product, but its weight was not found.

The Ash.

Five different portions of berries of about 2 grms. each were ashed in a small platinum dish. The first was examined for SiO_2, Fe_2O_3, Al_2O_3, CaO, and MgO; the second for alkalis; the third for SO_3; the fourth for P_2O_5; the fifth for manganese and chromium. The alkalis were determined by a modification of the J. Lawrance Smith method. It was impossible to make a CO_2 determination as the ash fused into a glassy solid. The burning fruit at first gave a sweet odour like hot toffy or molasses. This gave place to a mild odour of roasting apples, but it was soon obliterated by a penetrating odour of burning leaves which affected the eyes and nose.

The average weight of ash was 2·35 per cent of the fruit. The results are as follows:—

	Per cent.
Insoluble residue	0·08
Fe_2O_3	6·77
Al_2O_3	13·74
CaO	2·58
MgO	1·65
SO_3	4·50
P_2O_5	24·46
MnO	0·013
CrO	0·026
Na_2O	17·77
K_2O	23·25
Total	94·84

A portion of the residue after the sugar and oil extraction was thoroughly dried, and about 2 grms. ashed. The ash content was reduced to 1·35 per cent, a loss of nearly one-half. There was a much larger amount of smoke when it was burned. The only odour observed was that of damp burning leaves. The following determinations were made:—

	Per cent.
Insoluble residue	1·85
Fe_2O_3 and Al_2O_3	21·11
CaO	27·78
MgO	22·22
	73·96

Tests with both the sugar extract and the residue showed that the substances removed from the original fruit were principally alkaline phosphates, carbonates, &c.

The Proteins.

The total nitrogen was determined by the Kjeldahl method. About 2 grms. of the fruit were treated, and 0·14 per cent of nitrogen was found.

A portion of the fruit was crushed and boiled with distilled water for a few hours. The liquid resembled the juice from stewed prunes in colour and taste. A small amount of the liquid was heated with nitric acid, giving a light yellow colour, which became a light red when the solution was made alkaline. This indicated a small amount of albumen. Another portion of the liquid was tested to learn if sulphur was present in the albumen, but the amount of albumen was so small that no conclusion could be reached.

The fumes from heating the fruit alone or with soda-lime reacted alkaline to litmus.

The Acids.

Tests were made for many of the common organic acids, and malic by a number of different methods was found to be the predominating one. There was a slight trace of tannin. The reaction of the sugar solution and the sweet taste of the fruit itself indicate that the acids exist in small quantities.

Cornell College,
Mount Vernon, Iowa, April 1, 1911.

A PHYSICO-CHEMICAL STUDY OF MERCURY SODIUM ALLOYS OR SODIUM AMALGAMS.*

By ERNEST VANSTONE (B.Sc., Wales), 1851 Exhibition Research Scholar, University College of South Wales and Monmouthshire.

(Concluded from p. 201).

The Measurement of the Specific Volumes of Solid Mercury-sodium Alloys.

Maey, in 1899, determined the specific volumes of mercury-sodium alloys at room temperature. The concentrations of the amalgams varied from 0 to 80 per cent sodium. His method of applying the results to determine the composition of the various compounds involves the assumption that no appreciable contraction occurs on mixing sodium and mercury. This assumption is untenable, as it has been shown above that large contractions occur. The densities of a complete series of solid amalgams have been determined by a method similar to that employed by Maey, namely, by weighing the alloy suspended in petroleum. The amalgams were made as follows:—A piece of sodium was cut up under a mixture of light petroleum and ether; it was removed to a beaker containing liquid paraffin, which had been previously weighed. The beaker was again weighed, and the weight of the sodium obtained. It was then heated until the sodium fused, the requisite quantity of mercury added, the amalgam allowed to solidify, and the paraffin removed by washing with light petroleum.

Table VI.—*Specific Volumes in the Solid State. Temperature 17° C.*

Concentration.	Specific volume (observed).	Specific volume (calculated).	Contraction.	Percentage contraction.
98·13	0·88896	0·89811	0·00915	1·0188
96·81	0·80937	0·82144	0·01187	1·4450
91·82	0·58285	0·61592	0·03307	5·3692
85·82	0·42871	0·46791	0·03920	9·3347
84·63	0·40541	0·44715	0·04174	10·360
83·26	0·38030	0·42425	0·04395	10·420
82·81	0·37375	0·41714	0·04339	10·990
81·76	0·35742	0·40155	0·04413	11·957
78·36	0·31435	0·35704	0·04269	15·406
74·34	0·26615	0·31462	0·04847	16·422
72·26	0·24734	0·29594	0·04860	15·995
68·09	0·22153	0·26371	0·04218	15·969
65·19	0·20554	0·24460	0·03906	16·219
64·00	0·19893	0·23744	0·03851	18·774
59·53	0·17637	0·21329	0·03692	18·542
55·94	0·16018	0·19664	0·03646	17·641
55·19	0·15769	0·19342	0·03573	19·216
53·59	0·15092	0·18682	0·03590	19·714
50·37	0·13993	0·17419	0·03426	19·438
48·17	0·13416	0·16653	0·03237	21·231
46·92	0·12822	0·16278	0·03456	20·708
43·85	0·12154	0·15328	0·03174	19·411
38·46	0·11160	0·13848	0·02688	19·048
37·00	0·10914	0·13482	0·02568	18·558
32·92	0·10208	0·12534	0·02326	15·836
29·93	0·10013	0·11897	0·01884	13·683
26·79	0·09734	0·11277	0·01543	12·014
22·92	0·09301	0·10571	0·01270	7·3995
19·44	0·09248	0·09987	0·00739	6·1819
16·77	0·08954	0·09544	0·00500	9·043
100	1·0342			

The alloy was then weighed in a beaker containing paraffin, and again weighed when suspended in paraffin by means of a hair. All the data for the density determinations were thus obtained. The results are given in Table VI.

There is close agreement between the present values and those obtained by Maey.

* A Paper read before the Faraday Society, March 14, 1911.

The specific volume-concentration curve is smooth (Fig. 11), as in the case of the liquid alloys. The percentage contractions have also been plotted against concentrations. A discontinuous curve is obtained (Fig. 12) similar to the freezing point diagram; the breaks in this curve occur at concentrations agreeing approximately with those in that diagram. What has already been said concerning liquid alloys applies here also.

It will again be observed that the maximum contraction occurs at a concentration of 48 per cent sodium.

The compound $NaHg_2$ does not appear to be formed with very great contraction.

The Molecular Volumes of Compounds of Mercury and Sodium.

From the specific volumes of the solid amalgams we can calculate the molecular volumes of the various compounds. These are given in Table VII., in which v denotes the specific volume, M the molecular weight, and V the molecular volume.

In the fifth column are given the ratio molecular volume/sum of valencies or valency volume. Sodium has been taken as monovalent and mercury divalent.

Table VII.

I. Compound.	II. v.	III. M.	IV. V.	V. V/W	VI. V′ calculated.	VII. V′—V.
Na_3Hg..	0·275	269	73·97	14·70	86·12	12·14
Na_3Hg_2.	0·177	469	83·01	11·86	100·87	17·86
$NaHg$ ..	0·139	223	30·99	10·33	38·54	7·54
Na_7Hg_8 . ?	0·126	1761	221·83	9·64	284·57	62·69 ?
$NaHg_2$..	0·102	423	43·14	8·63	53·30	20 16
$NaHg_4$..	0·090	823	74·07	8·23	82·82	8·75

The atomic volume of sodium in the solid state at room temperature 18° C. is 23·786, that of mercury 14·759.

The molecular volumes have been calculated, and are given above in Column VI. In the seventh column are given the differences between the observed and calculated molecular volumes. These are the molecular contractions.

No relation can be traced between valency and volume, the ratio V/W gradually diminishing as we pass to compounds relatively richer in mercury. This is precisely the manner in which the ratio changes when calculated for organic halogen compounds or inorganic compounds. The ratio always increases as the proportion of the element of larger atomic volume increases, or if an element be replaced by another of larger atomic volume. This is shown in Table VIII.

Table VIII.

Compound.	V/W.
CH_2Cl_2	8·14
$CHCl_3$	10·56
CCl_4	12·96
C_6H_6	8·53
C_6H_5F	9·03
C_6H_5Cl	10·30
C_6H_5Br	10·78
C_6H_5I	11·69
PCl_3	11·66
PCl_5	12·89
$NaClO_4$	4·65
$KClO_4$	5·49
$RbClO_4$	6·13
$CsClO_4$	7·00

The Microscopic Investigation of Mercury-sodium Alloys.

The peculiar nature of the alloys under investigation—their low melting-points, their low degree of hardness, and the extreme rapidity with which they undergo oxidation—has hitherto prevented any microscopic work.

By forming the alloys in a vessel the base of which is a microscope cover glass, it has been found possible to observe the various changes in crystalline structure and to

Fig. 11.

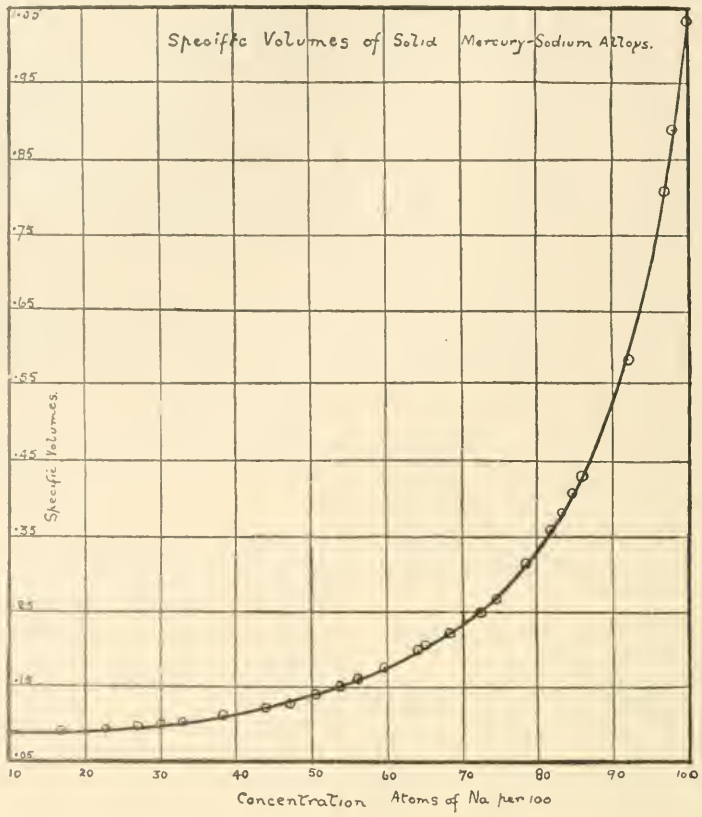
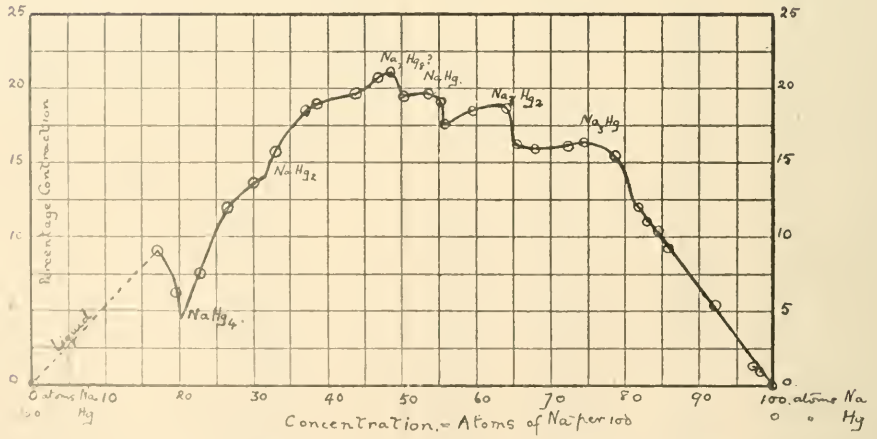


Fig. 12.



prepare micro-photographs. The alloys were first made in small beakers. A vessel was then made by cementing a small glass cylinder to a microscope cover glass. A small quantity of vaseline was then placed in the vessel, and the molten alloy poured into it. It was allowed to cool slowly, the vaseline solidified on the surface, thus preventing oxidation, and also permitting the vessel to be turned into any position.

The crystalline structure of the alloy could be plainly seen on looking at the base of the vessel, the alloy having crystallised on the microscope cover. Photographs were taken and are described below. No method of polishing or of etching the specimens was possible.

No. 1. Concentration 85 per cent sodium. This consists almost entirely of the eutectic mixture. The crystals are hexagonal plates.

No. 2. Concentration 75 per cent sodium. The crystals are mainly those of the compound Na_3Hg. They are large plates with the edges turned towards the microscope cover glass.

No. 3. Concentrations 65 per cent sodium. The crystals consist mainly of the compound Na_3Hg_2.

No. 4. Concentration 55 per cent sodium. Prismatic crystals of the compound NaHg.

No. 5. Concentration 49 per cent sodium. A microphotograph of a small portion of the alloy, as seen through the bottom of a small thin glass beaker in which the alloy was made, has been taken. Attempts to prepare a specimen in the same manner as the others always produced a surface covered with air-bubbles. The crystals consisted of flat plates of the compound formed in the small branch of the thermal diagram. The composition of the compound is uncertain; Na_7Hg_8 has been suggested.

No. 6. Concentration 25 per cent sodium. This alloy has a high melting-point and only oxidises slowly. It was made in a small glass beaker, the alloy removed, quickly polished with cotton-wool, and the photograph taken. The crystals are those of the compound $NaHg_2$.

No. 7. Concentration 15 per cent sodium. The crystals are long prisms of the compound $NaHg_4$.

Summary and Conclusion.

The methods of preparing the amalgams described in the present work should lead to their wider application in chemical operations, particularly to reduction processes in organic chemistry. Amalgams containing large quantities of sodium should be really more convenient than sodium itself, on account of their greater density, which would enable them to remain at the bottom of the vessel.

An alloy containing 85 per cent sodium is liquid at 21·4° C., and should be especially useful.

Further experiments are in progress on the electrical conductivities of the solid mercury-sodium alloys.

1. The investigation of the freezing-points of sodium amalgams has confirmed to a large extent the work of Schüller. There are, however, differences both in temperatures and concentrations at which the breaks in the thermal diagram occur. Six compounds are shown to be formed having compositions indicated by the following formulæ:—Na_3Hg, Na_3Hg_2, $NaHg$, Na_7Hg_8?, $NaHg_2$, $NaHg_4$.

2. The specific volumes of the amalgams in the liquid state have been determined. Specific volume-concentration curves are smooth, and do not give evidence of the existence of compounds in the liquid state.

3. The effect of mixing sodium and mercury is to produce a contraction in volume which increases until the proportion of sodium reaches a concentration of 48 per cent; the contraction is a maximum at this point, and diminishes steadily as the mercury concentration increases. Contraction-concentration curves are given. These show discontinuities similar to those in the freezing-point diagram.

4. The specific volumes of liquid sodium at temperatures of 110° C., 184° C., and 237° C., have been determined. The relation between volume and temperature over this range is approximately linear.

5. The specific volumes of solid amalgams have also been determined at room temperature. A smooth curve is obtained when specific volumes are plotted against concentrations. A discontinuous curve resembling the freezing-point diagram is obtained when percentage contractions are plotted against concentrations.

6. Simple methods of preparing sodium amalgams are described.

7. The crystalline structure of the various amalgams has been studied under the microscope. Micro-photographs have been obtained. The results confirm the freezing-point investigation.

8. No relation can be traced between molecular volumes of mercury-sodium compounds and valency.

In conclusion, I wish to thank Sir William Ramsay for the great interest he has taken in the work and for his constant advice, also Dr. Desch, of the University of Glasgow, for many valuable suggestions, and Assistant Professor A. W. Porter for much help in the photographic portion of the work.

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.*

First Paper.—The Analysis of Neodymium Chloride.

By GREGORY PAUL BAXTER and HAROLD C. CHAPIN

(Continued from p. 197).

The Absorption Spectrum of Aqueous Solutions of Neodymium Salts.

The absorption spectra of two of the purest fractions, 2929 and 2931, were examined visually with a Hilger wave-length spectroscope. While no very great accuracy is claimed for the measurements, it is probable that the values are correct within one-millionth of a millimetre, for the spectroscope is capable of nearly ten times this accuracy for wave-lengths in the neighbourhood of λ 500.

In the first two columns of the following table are given the values for the maxima of absorption observed during the gradual dilution of very concentrated slightly acid solution of the nitrates, each value having been obtained in the most dilute solutions in which the band could be observed. The spectra of the two fractions were identical.

The band λ 580 can be seen only at certain medium concentrations, while the band λ 547 is visible only with very concentrated solutions. The praseodymium band λ 444 also was faintly visible only in the most concentrated solutions. The two bands λ 580 and λ 547 disappear if the nitrate is changed to chloride; otherwise the nitrate and chloride give maxima in essentially the same positions, although the relative intensities of the bands are somewhat different in the two cases.

Baxter and Chapin fractions 2929 and 2931. (1909).	Forsling and Holmberg (1907).	Rech and Muthmann (1906).	Auer von Welsbach (1903).
—	—	—	745 to 725
689	689·5	—	687
679	677·5	679·6	678
673	672·0	670·8	673
636	636·0	636·6	635
628	627·8	628·6	629
625	625·4	624·8	626
622	621·7	622·2	622
587	—	586·5	—
583	—	583·2	583
580	—	580·8	—
578	578·8 to 578·0	578·5	579
575	575·4	575·4	579
574	573·5	573 6	575
571	571·6	571·7	572·5
547	—	—	567·5
531	532·3	532·0	532
525	—	525·4	525
521	521·6	522·2	522·7
520	520·4	520·5	521
—	—	514·5	—
512	512·4	512·2	511·7
509	508·7	508·9	508·3
487	489·0 to 486·0	488·0	—
480	479·9	479·8	—
475	474·8 to 474·2	475·4	475·4
469	468·7	469·0	469·6
461	461·0	461·1	461
444 Pr	—	444·2	—
433	433·0	434·2 ; 432·9	432
429	—	429·5 ; 428·1	—
427·5	427·1	427·2	426·5
418	418·3	418·2	417·8

The third, fourth, and fifth columns of the foregoing table represent the corresponding results obtained by

* *Journal o the American Chemical Society*, xxxiii., No. 1.

Forsling's from Holmberg's neodymium preparation (*Zeit. Anorg. Chem.*, 1907, liii., 83), by Rech from Muthmann's preparation (*Zeit. Wiss. Photographie, Photophysik, u. Photochemie*, 1906, iii., 411), and by Auer von Welsbach from his own material (*Zitzungsber. Akad. Wiss. Wien*, 1903, cxii., 1037). The last were taken from the drawings which were Auer's only published record, and since they are subject to two personal errors are less exact than the others. Being obtained, however, from very carefully prepared material, they should represent at any rate the number and the general location of the bands in the neodymium spectrum.

While some of these bands are sharp, and appear in the same positions in solutions of various concentrations, others fade away gradually on the edges, and sometimes have their maxima shifted by changes in the concentration. Consequently the disagreement as to the exact positions of bands is due in many cases merely to differences in the conditions of observation. Furthermore, Forsling and Rech used chloride solutions, whereas Auer von Welsbach and the writers used nitrate solutions. On the whole, the agreement between the different sets of values is very satisfactory. The bands between λ 587 and λ 571 are too close together to be distinguished from one another under any but the most favourable conditions. The double band λ 575 and λ 574 in particular separates only under rather limited conditions. The band at λ 579 in one of Auer's drawings may be intended to represent two lines at λ 580 and λ 577, and is thus interpreted by Kayser. Auer's band λ 567·5 appears very faintly in but one of his four drawings. There is a complete absence of shadow at this point in another drawing which represents a more concentrated solution, and which one would expect consequently to show the band. It is possible therefore that its appearance in the first print was merely accidental. The band λ 525 in concentrated solutions merges with λ 522 and in dilute it becomes invisible, so that it is not surprising that it was not observed by Forsling and Holmberg. The band λ 514·5, given by Rech alone, is coincident with no prominent band of any other rare earth, nor could it be detected in any of our preparations. The band λ 488, which both Forsling and Rech observed, as, has already been stated, can be seen only with very strong absorption. This is doubtless the reason that it was not observed by Auer.

The presence or absence of the predominant impurities, praseodymium, cerium, lanthanum, and samarium, in our best material has already been discussed. It is of some interest to consider other earths having prominent absorption bands in the visible spectrum. (The following data are obtained from drawings by Urbain, *Journ. Chim. Phys.*, 1906, iv., 31, 105, 232, 321). Since none of these could have been present in quantity, their absorption bands obviously could be found only in concentrated solutions. The marked broadening and running together of the neodymium bands in concentrated solutions makes the detection of bands due to impurities difficult, except when these occur in regions in the spectrum comparatively free from neodymium bands. Of the three strong erbium bands λ 650, λ 540, and λ 522, the last two are completely masked by the neodymium in concentrated solution. The band λ 650, however, occurs in a region favourable for observation, and could not be detected even in the most concentrated solution. In the case of holmium the three strongest bands, λ 639, λ 535, and λ 485, all fall within the limits of neodymium bands at high concentrations. There was no evidence of the strongest, λ 535, in solutions of average concentrations. The strongest dysprosium band λ 451, which falls just within the broad neodymium band λ 484—λ 453, as it appeared in our most concentrated solutions, could not be detected. The terbium band λ 488 practically coincides with the neodymium band 487, which could be seen in our preparations only at the highest concentrations. Since the band could be seen of the same intensity in all our preparations, it is improbable that it represents an impurity of terbium. The sharp thulium band λ 700 does not fall within the limits of any neodymium band, and we could find no evidence of its presence. Since the absorption of europium solutions in the visible spectrum is faint, and since all the stronger bands are masked completely by the bands of a concentrated neodymium solution, we have no spectroscopic evidence concerning the absence of this element. It may be added that, even in the extreme fractions of our crystal series, we could not detect the presence of any of these rarer elements. Further study of the absorption spectrum of neodymium is planned with the aid of a large quartz spectrograph, which has recently become available for us.

The Preparation of Neodymium Chloride.

The neodymium oxide fractions prepared as above were converted to chloride as follows:—Fractions 1302 and 1614 were dissolved in the purest nitric acid in platinum vessels, the solutions were filtered, and the oxalate was precipitated from acid solution by means of the purest oxalic acid. After the oxalate had been washed by decantation and drained by suction upon a porcelain Gooch crucible employing a small disc of filter-paper in place of an asbestos mat, the salt was dried and ignited in a platinum dish over a blast lamp. The oxide was dissolved in a quartz dish in hydrochloric acid which had been distilled with the use of a quartz condenser, and the chloride was three times crystallised with centrifugal drainage in platinum Gooch crucibles in each case (Baxter, *Journ. Am. Chem. Soc.*, 1908, xxx., 286). The crystal yield was brought to a maximum by treating the solution at 0° with hydrochloric acid gas obtained by warming concentrated solutions of the acid and led to the solutions through a quartz tube. Drying over sulphuric acid in a vacuum desiccator and powdering in an agate mortar completed the preparation for the final dehydration and analysis.

On account of the small quantity of material in each fraction of the final series, adjacent fractions were combined. The combinations actually analysed were 2923—2924, 2926—2927—2928, 2932—2933, and 2936—2937. A suspicion of contamination by platinum during the ignition of the oxides in platinum led to a slight change in the purification of these fractions. The original oxide was dissolved in hydrochloric acid in a quartz dish, and hydrogen sulphide, generated by the action of sulphuric acid on ferrous sulphide and thoroughly scrubbed with water, was passed into the hot slightly acid solution. A slight black precipitate of platinum sulphide was formed in every case. The oxalate was precipitated from the filtered and boiled solution, and was collected and dried as before. In the ignition of this oxalate an electrically heated quartz muffle, kindly loaned to us by Dr. H. H. Willard, was used. Since the temperature of the muffle was very uniform, a lower temperature could be employed for the decomposition of the oxalate. The product of decomposition, which contained a large proportion of carbonate when obtained in this way, was dissolved in hydrochloric acid in a quartz dish and was crystallised as before. The first mother-liquor, which in the case of fractions 1302 and 1614 had been slightly tinged with yellow, was in the case of all the other fractions free from such evidence of dissolved platinum.

The Preparation of Pure Silver.

Pure silver was prepared by methods which have already been found to be very effective. Since these methods have been described in detail several times in papers from this laboratory, only a brief outline of the processes is given here (see especially Richards and Wells, *Pub. Carnegie Inst.*, 1905, No. 28, 16; *Journ. Am. Chem. Soc.*, xxvii., 472). Crude silver was dissolved in nitric acid, precipitated as chloride, reduced with alkaline invert sugar, and fused on charcoal. After cleansing by scrubbing with sand and etching with nitric acid, the buttons were again dissolved in nitric acid and the metal was precipitated from solution with ammonium formate. The thoroughly washed product was fused with a blowpipe upon a crucible of the purest lime. Electrolytic deposition with silver

nitrate as the electrolyte and with a dissolving anode of the pure silver buttons followed, and the electrolytic crystals were fused in a current of pure hydrogen on a boat of the purest lime. The resulting bars of metal were first cleansed with nitric acid and then were sawed into pieces of a convenient size with a fine jeweller's saw. After the fragments had been etched with nitric acid until free from surface contamination with iron from the saw, they were thoroughly washed with ammonia and pure water, and finally heated to about 300° in a vacuum. The silver was preserved in a desiccator over solid potassium hydroxide.

Pure silver nitrate was prepared by crystallisation of the commercial product until free from chloride. That used in analyses 6, 7, 8, and 15 was a portion of material purified by Dr. Grinnell Jones for work upon the atomic weight of phosphorus (Baxter and Jones, *Proc. Am. Acad.*, 1909, xlv., 137; *Journ. Am. Chem. Soc.*, xxxi., 298).

In the preparation of reagents the precautions usual in exact work were taken. The ordinary distilled water of the laboratory was twice re-distilled, once from alkaline permanganate and once alone, through block-tin condensers. Hydrochloric and nitric acids were distilled through quartz condensers, in the case of the hydrochloric acid the first and last running being rejected, in the case of the nitric acid two distillations being carried out, the first third being rejected in each distillation. By careful tests it was shown that nitric acid distilled in this way does not contain more than the merest trace of chlorine, if the original acid is nearly free from the latter element.

Quartz or platinum utensils were employed wherever glass would have introduced objectionable impurities, and electrical heaters were used whenever the products of combustion of illuminating gas were to be avoided. In the crystallisation of solids centrifugal drainage was always used to assist in the mechanical removal of mother-liquor from crystals, except in the fractional crystallisation of the neodymium material, where it would have been of little assistance.

The Drying of the Neodymium Chloride.

The drying of the neodymium chloride for analysis presented several difficulties. Matignon (*Comptes Rendus*, 1901, cxxxiii., 289) states that if the chloride is first completely dehydrated and then fused in a current of dry hydrochloric acid gas, the product is completely soluble in water. Our earlier experiments did not confirm this statement, for in several instances salt which apparently had been very completely dried, after fusion in a current of hydrochloric acid gas was found to contain a considerable amount of basic salt. Since, however, material which had been dried at temperatures slightly below the melting-point of the anhydrous salt gave absolutely clear solutions, the expedient was adopted of drying the salt for analysis as completely as possible without fusion, with the expectation of determining the water in subsequent experiments. During later experiments for determining the residual water it was found that the preliminary drying had not been effective in the earlier experiments, and that salt which has been dried as for analysis and then fused in a current of hydrochloric acid gas does give a perfectly clear solution. This information was unfortunately acquired too late to be of direct use in preparing the salt for analysis. Since, however, the dried but unfused salt was found to contain a constant very small proportion of moisture, and since a correction was applied for this moisture, no appreciable error could have been introduced by the incomplete drying. It is hoped, nevertheless, before long to institute further analyses with material which has been fused.

The apparatus employed in the drying of the neodymium chloride was essentially that used by numerous investigators in this laboratory for the dehydration of chlorides. Hydrochloric acid gas was generated by the action of concentrated sulphuric acid upon concentrated hydrochloric acid, and was dried by passage through five towers about 30 cc. long and 4 cc. in diameter filled with glass beads moistened with concentrated sulphuric acid. Nitrogen was prepared by Winklyn's method of passing air through a concentrated ammonia solution and then over hot copper. The excess of ammonia was removed and the nitrogen was purified and dried by passing over dilute sulphuric acid, silver nitrate solution, solid caustic potash, concentrated sulphuric acid, and re-sublimed phosphorus pentoxide. Nitrogen prepared in this way always contains hydrogen (our attention was first called to this fact by Dr. R. C. Wells), produced by the catalytic decomposition of the excess of ammonia in passing over the hot copper, in quantities which vary with the excess of ammonia and the temperature of the copper, as well as the length of the copper layer and the speed of the gases. The hydrogen could not have had any effect upon the neodymium chloride, however, and was an advantage in preventing the attacking of the platinum boat. Air was purified and dried by reagents similar to those used in the purification of the nitrogen. The hydrochloric acid apparatus was constructed wholly of glass, and the nitrogen and air purifying trains had short rubber connections only at the beginning. Any one of these gases or any desired mixture could be delivered through the tube in which the boat containing the salt was placed. This tube could be heated to constant temperatures in an oven consisting of two superimposed solid aluminium blocks (Baxter and Coffin, *Proc. Am. Acad.*, 1909, xliv., 184; *Journ. Am. Chem. Soc.*, xxxi., 206).

According to Matignon (*Comptes Rendus*, 1901, cxxxiii., 289), at about 105° neodymium chloride loses five of its six molecules of water of crystallisation rapidly, while the sixth molecule appears at 160°. We have determined the melting-point of the hexahydrated chloride (made from fraction 2931) to be 124°. Thus the drying of the chloride may be caused to take place by a process of double efflorescence, a condition very favourable for the complete elimination of the water. Richards (*Zeit. Phys. Chem.*, 1903, xlvi., 194) has pointed out that a hydrated salt dried wholly by efflorescence can be freed from moisture much more effectively than one which has been allowed to melt during the dehydration, hence care was taken to keep the temperature below 124° until the greater part of the water had been expelled.

The powdered crystals of neodymium chloride were placed in a platinum boat which had been previously weighed in a weighing bottle, and the boat was heated in a current of mixed nitrogen and hydrochloric acid gases at gradually increasing temperatures. The boat was contained in a hard glass tube which formed part of a "bottling apparatus" (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxii., 59), and this in turn was attached to the systems for purifying the various gases. The temperature was kept below 124° until the larger portion of the water had been expelled. Then it was gradually raised to 200°, and finally the salt was heated at about 330° for one hour in a current of pure hydrochloric acid gas. During the heating there was never the slightest appearance of melting. In the first five analyses the final temperature was higher than in the subsequent ones, and was not far below the fusing point of the anhydrous salt. After the tube had been allowed to cool, the hydrochloric acid was displaced by nitrogen and finally by air, and the boat was transferred to the weighing-bottle without exposure to moist air by means of the bottling apparatus. After long standing in a desiccator near the balance the boat and contents were weighed.

(To be continued).

Isosparteïn. A Case of Nitrogen Stereo-isomerism.—Charles Moureu and Amand Valeur.—With methyl iodide isosparteïn yields two distinct mono-iodomethylates, the α and α' compounds. Since by the decomposition of the two corresponding methyl hydrates the same unsaturated base is formed, it follows that the two iodomethylates differ from one another only as regards the arrangement in space of the methyl residue and the atom of iodine, with reference to the same nitrogen atom.—*Comptes Rendus*, clii., No. 9.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1911.

The Duke of Northumberland, President, in the Chair.

The Annual Report of the Committee of Visitors for the year 1910, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read. Thirty-nine new Members were elected in 1910. Sixty-one Lectures and seventeen Evening Discourses were delivered in 1910. The books and pamphlets presented amounted to about 239 volumes, making with 604 volumes (including periodicals bound) purchased by the Managers, a total of 843 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committee of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—John B. Broun-Morison; Dr. John Mitchell Bruce; Dr. Henry E. Armstrong; The Right Hon. Sir Henry Burton Buckley; Sir John Wolfe Barry; The Right Hon. Earl Cathcart; Dr. Donald William Charles Hood; Henry F. Makins; Sir Francis Laking Bart.; Alexander C. Ionides; Robert Mond; Dr. Rudolph Messel; The Hon. Charles A. Parsons; The Right Hon. Sir James Stirling; and Alexander Siemens.

Visitors—Henry Edmunds; Sir Frederick Fison, Bart.; William A. T. Hallowes; Dr. Arthur Croft Hill; John William Gordon; H. Robert Kempe; Major-General Sir Coleridge Grove; Charles Edward Groves; A. Kirkman Loyd; Frank K. McClean; Sir Charles Day Rose, Bart.; Major Percy A. MacMahon; William Stone; Emile R. Merton; and Harold Swithinbank.

CHEMICAL SOCIETY.

Annual General Meeting, March 23rd, 1911.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Dr. J. E. Mackenzie and Dr. R. H. Aders Plimmer were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The President presented the Report of the Council on the progress of the Society during the past twelve months; and the Treasurer made his statement as to the Society's income and expenditure for 1910. After some remarks by Dr. G. McGowan, Mr. A. W. Oke, and Dr. J. A. Voelcker, the adoption of the Report of the Council, together with the Balance Sheet and Statements of Accounts for the year ended December 31st, 1910, proposed by Mr. David Howard and seconded by Dr. F. B. Power, was carried unanimously.

A vote of thanks to the Auditors was proposed by the Treasurer, seconded by Dr. S. Smiles, and acknowledged by Dr. V. H. Veley.

Report of the Council.

Since our last Anniversary Meeting, we, in common with the rest of the Empire, have had to deplore the loss of the gracious Sovereign whose mission of peace among the nations did so much to foster the steady growth of science. In the address of condolence and of loyalty to his throne which his Majesty King George V. was pleased to receive from the Chemical Society, the Council ventured to call to mind, not only our indebtedness to his late Majesty, but also how much the progress of chemistry in Great Britain was due to the wisdom and foresight of the Prince Consort in the early days of the Society.

The Council is again in a position to report favourably on the progress of the Society, as indicated by an increase in the number of Fellows and in the list of papers communicated.

On December 31st, 1909, the number of Fellows was 3003. During 1910, 165 Fellows have been elected, and 5 were reinstated, the gross total thus being 3173. The Society has lost 18 Fellows by death; 38 have resigned; the election of 1 Fellow has become void, and 43 Fellows have had their names removed from the List of Fellows for non-payment of annual subscriptions.

The total number of Fellows, therefore, on December 31st, 1910, was 3073, showing a net increase of 70 over the preceding year.

The names of the deceased Fellows, with the dates of their election, are:—Richard Abegg (1906); Robert Barklie (1870); Robert Haslam Durward Benn (1904); Thomas Blackburn (1886); James Campbell Brown (1867); Benjamin Samuel Bull (1898); Michael Carteighe (1864); John Croysdale (1895); Frank Barnes Grundy (1903); Oscar Guttmann (1897); Edwin Bernard Hadley (1898); Angus Mackay (1877); Sir Walter Palmer, Bart. (1879); Arthur Gaved Phillips (1887); Richard Wightwick Roberts (1889); Thomas Bertram Udall (1876); John Tsawoo White (1889); Charles Hanson Greville Williams (1862).

The names of the Fellows reinstated by the Council in accordance with By-law IV. are as follows:—Edwin Bayles Atkinson; Frank Rawlinson Dudderidge; William French; Percy Walter Jones; Charles Frederic Townsend.

The number of Honorary and Foreign Members at the end of 1909 was 33. The Society has to mourn the loss of Prof. Stanislao Cannizzaro, Prof. Dr. Rudolf Fittig, and Geheim Rath Prof. Dr. Hans Landolt, who died during 1910.

It is with great pleasure that the Council offers its congratulations to the following gentlemen, who, during the past year, attained their Jubilee as Fellows of the Society:—Prof. Edward Divers, F.R.S.; Mr. Francis Sutton; Mr. Charles Henry Wood.

During the year 1910, 349 scientific communications have been made to the Society, 273 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1910 contains 2652 pages, of which 2601 are occupied by 270 memoirs, the remaining 51 pages being devoted to the Obituary Notices, the Thomsen Memorial Lecture, the Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 236 memoirs, which occupy 2133 pages.

The *Journal* for 1910 contains 4867 abstracts, which extend to 2032 pages, whilst the abstracts for 1909 numbered 4946, and occupied 2040 pages. The abstracts may be classified as follows:—

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	908	1634
Part II.		
General and Physical Chemistry ..		961
Inorganic Chemistry..		494
Mineralogical Chemistry..		118
Physiological Chemistry		700
Chemistry of Vegetable Physiology and Agriculture		287
Analytical Chemistry		673
	1124	3233
Total in Parts I. and II. ..	2032	4867

During the past year the Society has rejoiced in having the privilege of offering its congratulations and those of the whole chemical world to five of its Past-Presidents, who had completed upwards of fifty years' Fellowship of the Society, namely, Prof. W. Odling, the Right Hon. Sir Henry E. Roscoe, Sir William Crookes, Dr. Hugo Müller, and Dr. A. G. Vernon Harcourt. The Banquet held on Friday, November 11th, 1910, to do honour to these gentlemen will remain a notable event in the history of the Chemical Society. To the great regret of all, Sir Henry Roscoe was, owing to indisposition, unable to be present.

In order to render more complete the records and statistics of the Society, and to make them available to the Fellows at large, the Council has ordered the preparation of a complete chronological list of Fellows from the foundation of the Society in 1841.

Prof. Theodore W. Richards has been invited to deliver the Faraday Lecture, and the Council has pleasure in announcing that, through the courtesy of the Managers, an Extraordinary Meeting of the Society will be held on June 14th in the Lecture Theatre of the Royal Institution, where all the Faraday Lectures have been given. The title of the discourse will be announced in due course.

On behalf of the Society, the Council presented a Congratulatory Address to its Honorary and Foreign Member, Prof. Wilhelm Körner, on the occasion of his seventieth birthday.

By the death of Stanislao Cannizzaro, the Society has lost its Senior Honorary and Foreign Member, elected on June 19th, 1862. Sir William Tilden has accepted the invitation of the Council to deliver a Memorial Lecture in his honour.

The Council has further arranged for the following Memorial Lectures to be delivered: — Antoine Henri Becquerel (d. August 25th, 1908), by Prof. Ernest Rutherford, F.R.S.; Marcellin Berthelot (d. March 18th, 1907), by Prof. Harold B. Dixon, F.R.S.; Henri Moissan (d February 20th, 1907), by Sir William Ramsay, K.C.B., F.R.S.

In response to an appeal from the University of Toulouse for help in attempting to render good the almost complete destruction of the Science portion of its library by fire on October 27th last, the Council have decided to present the University with a number of volumes of the *Transactions* of the Chemical Society. It is unfortunately impossible for the Society on such an occasion as this to present a complete set of its publications, owing to the fact that many of the earlier volumes are out of print. A number of volumes of the *Transactions* has also been presented to the University of Manitoba, Winnipeg.

In December, 1909, the International Commission for the publication of Physical-chemical Constants invited the Society to assist in the work of the Commission by contributing towards the expenses of its work. After due consideration, the Council has decided to make a contribution of £10 out of the funds of the Society for the year 1911, at the expiry of which time the matter will receive further consideration.

An intimation has been received from the Secretary of the International Congress of Applied Chemistry that the Congress will meet in the first half of the month of September, 1912, the opening meeting to be held in Washington, and subsequent meetings of the Congress and its Sections in New York City.

Prof. A. Haller, on behalf of the Chemical Society of France, has invited the Chemical Society to co-operate in the formation of an International Committee to consider questions of chemical nomenclature and other matters, with a view to facilitate the reading of chemical researches published in different languages. Prof. Haller suggests that established Chemical Societies should appoint delegates to meet once or twice a year, and that questions considered at such meetings should be referred to and discussed by the several Societies independently, and then finally by the International Committee.

The Council has expressed its willingness to appoint delegates to serve on the International Committee, should such be formed.

The Chemical Society has during the past year received, through the kindness of Prof. G. Carey Foster, a copy of Richard Watson's "Pars Mettallurgica Institutium Chemicarum"; the Right Hon. Sir Henry E. Roscoe has presented a unique set of photograph portraits of Chevreul; and Mr. Ernest de la Rue has added to the collection of portraits one of the late Warren de la Rue, who was President of the Society during two periods, 1867-1869 and 1879-1880. Valuable presents of the Society's publications have also been received from Mr. J. McDougall and Dr. E. Cox Seaton.

During the year, 1918 books were borrowed from the Library, as against 1548 during 1909; of these 553 were issued by post, as compared with 347 in the preceding year.

The additions to the Library comprise:—163 books, of which 80 were presented, 431 volumes of periodicals (representing 236 journals), and 141 pamphlets, as against 142 books, 418 volumes of periodicals (representing 243 journals), and 80 pamphlets last year.

Although the income of the Society for the year 1910 falls short of its expenditure by no less than £147 6s. 4d., this need hardly cause any serious alarm, nor must it be assumed that henceforth this must be our usual condition. This undesirable result on the year's working has been brought about by several causes acting simultaneously.

The increase in income for 1909 over that for 1908 was £252, whilst that for 1910, from all sources, only exceeded that for 1909 by £59 17s. 10d., the respective amounts being £7447 5s. 10d. for 1910, and £7387 8s. for 1909. Whilst our income has improved so little, the expenditure has risen from £7028 3s. 5d. to £7594 12s. 2d., an increase of £566 8s. 9d. As mentioned earlier in the Report, the volume of our *Transactions* has increased by more than 500 pages; that is, roughly, a quarter more than last year. This is reflected in the increase of £399 7s. 5d. in the cost of the Journal alone. Administrative expenses have also increased much more than usual, owing to certain expenses which had to be met this year of an abnormal character, and which are not likely to recur for several years. The total increase under this head is £188 4s. One other item which calls for remark is the large deficit on the Dinner Account, which has to be met from the funds of the Society. This time it amounts to £91 15s. 2d., but it ought to be pointed out that this is unusually high, and is due, in part, to the postponement of the Banquet from May 26th until November 11th, necessitated by the death of King Edward on May 8th. In view of the narrow margin between our income and expenditure it is to be hoped that some satisfactory method of avoiding this drain upon our resources may be devised and adopted in arranging for the next Anniversary Dinner, which, in the ordinary course, should fall in March, 1913.

Since the Officers of the Society have undertaken the management of the advertisements a profit of £75 12s. 5d. has resulted, whereas last year our net gain from this source was a little under £10.

The snapping of one of the links with the past, which all must regret, has been brought about by the death, in September, of Mrs. Emily Hall. The pension of £30 a year, granted in 1903 to Mrs. Hall on the death of her husband, Mr. Josiah Hall, for twenty-five years the courteous collector for the Society, thus lapses.

The income of the Research Fund exceeds the expenditure by £29 6s. 5d. This is due chiefly to the balances of grants made in previous years which remained unexpended having been returned by the grantees. These amount to £46 2s. 1d., and this sum is now available for redistribution. The normal income of the Fund is £344, and a sum of £371 was divided amongst forty-eight applicants in amounts ranging from £5 to £20

A vote of thanks to the Treasurer, Hon. Secretaries, Foreign Secretary, and Council for their services during the

past year was proposed by Mr. A. D. HALL, seconded by Mr. J. SPILLER, and acknowledged by Dr. J. J. DOBBIE.

The PRESIDENT then delivered his Address, entitled, "On the Initiation and Propagation of Explosions." Sir WILLIAM TILDEN proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*; the motion was seconded by Sir WILLIAM RAMSAY, and carried with acclamation, the PRESIDENT making acknowledgment.

The Scrutators then presented their Report, and the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year:—

President—Percy F. Frankland, Ph.D., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; H. B. Dixon, M.A., Ph.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; R. Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; The Rt. Hon. Sir Henry E. Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William A. Tilden, D.Sc., F.R.S.

Vice-Presidents—G. T. Beilby, LL.D., F.R.S.; J. Norman Collie, Ph.D., F.R.S.; M. O. Forster, D.Sc., Ph.D., F.R.S.; A. Liversidge, LL.D., F.R.S.; W. J. Pope, M.A., F.R.S.; J. Walker, D.Sc., Ph.D., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—A. W. Crossley, D.Sc., Ph.D., F.R.S.; G. T. Morgan, D.Sc.

Foreign Secretary—Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council—W. A. Bone, D.Sc., Ph.D., F.R.S.; W. R. Bousfield, M.A., K.C.; Adrian J. Brown, M.Sc.; J. B. Cohen, Ph.D., B.Sc.; C. F. Cross, B.Sc.; C. E. Groves, F.R.S.; A. R. Ling; A. McKenzie, M.A., D.Sc., Ph.D.; Hugh Marshall, D.Sc., F.R.S.; J. C. Philip, M.A., D.Sc., Ph.D.; Sir Boverton Redwood, D.Sc.; A. E. H. Tutton, M.A., D.Sc., F.R.S.

Ordinary Meeting, April 6th, 1911.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

THE PRESIDENT made the following announcements:—

(*a*) That the Council had appointed the following Committees for 1911-1912:—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, Sir Edward Thorpe, Sir William Tilden, and the Officers.

House Committee—Messrs. W. R. Dunstan, R. Messel, J. E. Reynolds, J. M. Thomson, Sir Edward Thorpe, Sir William Tilden, and the Officers.

Library Committee—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, R. Meldola, E. J. Mills, J. C. Philip, J. M. Thomson, (Chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

Publication Committee—Messrs. J. N. Collie, B. Dyer, M. O. Forster, C. E. Groves, J. T. Hewitt, A. McKenzie, J. C. Philip, Sir William Ramsay, and the Officers.

Research Fund Committee—Messrs. H. B. Baker, G. T. Beilby, W. R. Bousfield, J. N. Collie, H. B. Dixon, A. Liversidge, R. Meldola, Sir Alexander Pedler, W. J. Pope, J. E. Reynolds, and the Officers.

(*b*) That the Faraday Lecture would be delivered on Wednesday, June 14th, 1911, at 8 p.m., by Prof. Theodore W. Richards, in the Lecture Room of the Royal Institution.

(*c*) That Sir William A. Tilden had been appointed by the Council to act as Delegate of the Society on the occasion of the Celebration of the 500th Anniversary of the Foundation of St. Andrew's University.

Certificates were read for the first time in favour of Messrs. Ernest Andrew Atkins, 71, East Hill, Wandsworth, S.W.; George Arthur Bradshaw, M.Sc., 28, Raymond Street, Bury; Arthur Frederick Clarke, 12, York Avenue, Gillingham; Charles Ernest Cooke, 35, Sebert Road, Forest Gate; Edgar Harold Gardner, 34, Salisbury Avenue, Colchester; Rowland Lewis Goold, 5, Corporation Street, Birmingham; Edward Lionel Joseph, 96, Victoria Street, S.W.; Richard William Merriman, M.A., 244, Victoria Park Road, S. Hackney.

Of the following papers, those marked * were read:—

*87. "*The Constituents of Rhubarb.*" By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

The material employed for this investigation consisted of the best quality of sun-dried "Shensi" rhubarb. An alcoholic extract of the drug, when distilled with steam, yielded small amounts of palmitic and chrysophanic acids together with a hexoic acid and some essential oil.

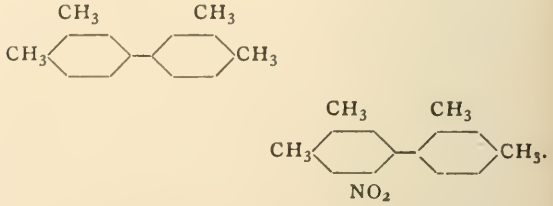
The portion of the extract, which was soluble in water, yielded cinnamic and gallic acids, rhein, emodin, aloe-emodin, emodin monomethyl ether, chrysophanic acid, and a new anthraquinone derivative, $C_{17}H_{10}O_6$ (m. p. 295—297°), which it is proposed to designate *rheinolic acid*. It yielded, furthermore, a crystalline mixture of the glucosides of rhein, emodin, aloe-emodin, emodin monomethyl ether, and chrysophanic acid, dextrose, lævulose, tannin, and an amorphous, non-glucoside resin. This resin, on hydrolysis, gave small amounts of gallic and cinnamic acids, rhein, emodin, aloe-emodin, emodin monomethyl ether, and chrysophanic acid, together with a new *compound*, $C_{14}H_{12}O_3$ (m. p. 256°), which is probably a *trihydroxydihydroanthracene*.

The portion of the extract undissolved by water yielded a trace of a hydrocarbon (m. p. 64°); a phytosterol (verosterol), $C_{27}H_{46}O$; a mixture of fatty acids, consisting of palmitic, stearic, oleic, linolic, and linolenic acids, both free and combined; rhein, rheinolic acid, emodin, aloe-emodin, emodin monomethyl ether, chrysophanic acid, and a trace of a substance which did not fuse at 340°, but yielded an acetyl derivative, melting at 335°. It also gave some amorphous products, and a further quantity of the crystalline mixture of the glucosides of the anthraquinone derivatives.

Of the anthraquinone derivatives, only aloe-emodin and chrysophanic acid had any purgative action, the mixture of glucosides being quite inert. The chief purgative principle is the above-mentioned non-glucosidic resin.

*88. "*6-Nitro-3 : 4 : 3′ : 4′-tetramethyldiphenyl.*" By ARTHUR WILLIAM CROSSLEY and CHARLES HERBERT HAMPSHIRE.

In continuation of experiments already described (*Proc.*, 1909, xxv., 162), the nitro-group has been eliminated from the nitrotetramethyldiphenyl prepared by the action of nitric acid on *o*-xylene, and the resulting tetramethyldiphenyl has been proved identical with 3 : 4 : 3′ : 4′-tetramethyldiphenyl:—



The latter hydrocarbon has been synthesised from 4-iodo-*o*-xylene under the influence of copper powder.

No direct evidence is forthcoming as to the position of the nitro-group, but indirect evidence supports the conclusion that it occupies position 6.

*89. "*Diphenylene, a New Aromatic Hydrocarbon.*" (Part I.). By James Johnston Dobbie, John Jacob Fox, and Arthur Josiah Hoffmeister Gauge.

Diphenylene, $C_6H_4{:}C_6H_4$, was prepared by the prolonged action of sodium on 2 : 2'-bibromodiphenyl (melting at 81°) dissolved in dry ether. The yield of the crude material is practically quantitative. This hydrocarbon dissolves readily in the usual organic solvents, and is best crystallised from light petroleum or alcohol; from such solutions it separates in flat prisms, melting at 74·5—75°. It closely resembles diphenyl in appearance and odour, but differs in melting-point. When mixed with diphenyl, its melting-point is depressed several degrees. Its absorption spectrum shows considerably greater general absorption than that of diphenyl.

The analysis and molecular weight determinations gave results agreeing with the formula $C_{12}H_8$.

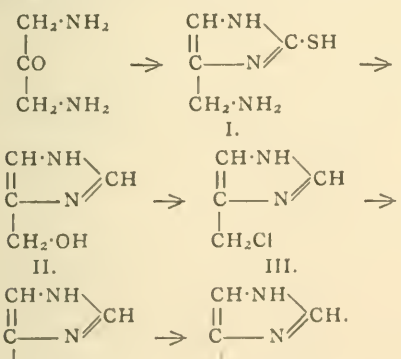
Discussion.

The President pointed out that benzene was usually stated to yield some phthalic acid on oxidation; it was therefore very remarkable that the authors should have found that diphenyl did not. Possibly the benzene used in the experiments on which the statement was based was not really pure.

*90. "*A New Synthesis of 4(or 5)-β-Aminoethylglyoxaline, one of the Active Principles of Ergot.*" By Frank Lee Pyman.

The following synthesis of 4(or 5)-β-aminoethylglyoxaline affords a convenient method for its preparation.

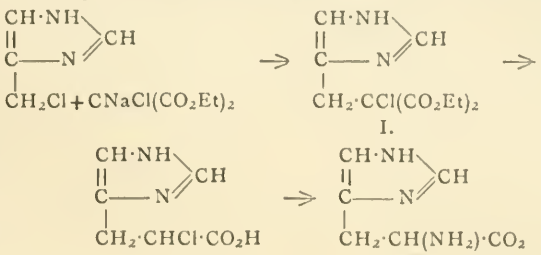
Diaminoacetone dihydrochloride when heated with potassium thiocyanate yields 2-*thiol*-4-(*or* 5)-*aminomethylglyoxaline* (I.) [m. p. 188° (corr.)], which on oxidation with nitric acid gives 4(or 5)-*hydroxymethylglyoxaline* (II.) [m. p. 93—94° (corr.)]. The hydrochloride of the latter is converted by phosphorus pentachloride into 4(or 5)-*chloromethylglyoxaline hydrochloride* (III.) [m. p. 144—145° (corr.)], and this, when suitably treated with potassium cyanide, gives rise to 4(or 5)-*cyanomethylglyoxaline* (IV.) [m. p. 138—140° (corr.)]. The latter base, on reduction with sodium and alcohol, yields 4(or 5)-β-aminoethylglyoxaline (V.).



A number of salts of these compounds, and several derivatives obtained as by-products in the various stages of the synthesis, were also described.

*91. "*The Synthesis of r-Histidine.*" (Preliminary Note). By Frank Lee Pyman.

4(or 5)-Chloromethylglyoxaline hydrochloride, of which the synthetical preparation is described in the preceding communication, is a valuable compound for the synthesis of substances containing the glyoxaline complex, for it reacts readily with ethyl sodioacetoacetate, ethylsodio malonate, and similarly constituted compounds, forming the corresponding 4(or 5)-glyoxalinemethyl ($C_3H_3N_2{\cdot}CH_2-$) derivatives. By the use of this salt, the synthesis of *r*-histidine has been effected as follows:—4(or 5)-Chloromethylglyoxaline hydrochloride and ethyl sodiochloromalonate readily condense, yielding *ethyl* 4(or 5)-*glyoxalinemethylchloromalonate* (I.), of which the *sesquioxalate*, $(C_{11}H_{15}O_4N_2Cl)_4(C_2H_2O_4)_3$, melts and decomposes at 176° (corr.). This base, on hydrolysis with 20 per cent hydrochloric acid, gives r-α-*chloro*-β-*glyoxaline*-4(or 5)-*propionic acid* (II.) [m. p. 201° (corr.)], which, when heated with strong ammonia at 110°, yields *r*-histidine (*r*-α-amino-β-glyoxaline-4(or 5)-propionic acid, (III.) [melting and decomposing at 283° (corr.)], identical in all respects with that obtained by racemising the naturally-occurring amino-acid *l*-histidine.



(To be continued).

NOTICES OF BOOKS.

New Ideas on Inorganic Chemistry. By Dr. A. Werner, Professor of Chemistry in the University of Zurich. Translated with the Author's sanction from the Second German Edition by Edgar Percy Hedley, Ph.D., A.R.C.Sc.I., Lecturer and Demonstrator in Chemistry, University of Birmingham. London, New York, Bombay, and Calcutta: Longmans, Green, and Co., 1911. (7s. 6d.).

This translation of the second edition of Dr. Werner's "New Ideas on Inorganic Chemistry" will be welcomed by those who have made use of the first edition published in 1905. The book has been practically re-written, and much additional matter has been added. The chief object of the revision has been the elaboration of the problem of valency, "thus to lay a foundation upon which in the near future it will be possible to build a consistent doctrine of valency." The new sections include the Theory of Bases and Acids, Theory of Hydrolysis, Constitution of Polynuclear Metallic Ammino-complexes, and Theory of Inner Metallic Complex Salts.

In the first section, "The Elements," the author discusses the recent researches of Ramsay on radio-active substances, and the production of lithium salts by the action of radio-active emanation on solutions of copper salts, the conception of meta-elements and the rare earths, and the periodic system, where a new scheme is suggested based only upon the chief characteristics of the elements.

A valuable feature in the book is the introduction of copious references to the literature involved, making it particularly useful to workers in inorganic chemistry. The translator in his preface characterises the work as a "veritable mine of suggestion for research on inorganic chemistry"; and by the original manner in which the subject is presented, and the lucidity of the expositions, there is little doubt that the second edition will be as greatly appreciated as was the first.

Crystallography and Practical Crystal Measurement. By A. E. H. Tutton, D.Sc., M.A. (Oxon.), F.R.S., A.R.C.Sc. London: Macmillan and Co., Ltd. 1911. (30s. net).

In this volume of 946 pages the author has endeavoured with a large measure of success to embrace both the practice and theory of crystallography. The unique

feature of the work is that, in addition to the exposition of the science of crystallography aided by practical demonstration and drawings, the student is conducted step by step through a mass of original investigation, much of which is published for the first time. The author has avoided complicated mathematical treatment; all the necessary calculations of crystal angles, and elements, as well as the physical constants, requiring only an ordinary acquaintance with simple trigonometry and the use of logarithms.

The illustrations of the figures of crystals are from the author's own drawings, and the numerous pieces of apparatus are from specially prepared woodcuts; the interference figures afforded by crystal plates in polarised light are reproductions of photographs taken in the author's laboratory, and as the number of the illustrations amount to over 700 some idea can be formed of the magnitude of the labour involved in the preparation of a work of this description.

The book is divided into two sections, Part I., Morphological, containing thirty-three chapters, and Part II., Physical, with twenty-two chapters. The last chapter includes an account of the liquid crystals of Lehmann, with instructions for their study by observation or screen projection.

At the conclusion of his "Introduction" the author expresses his gratitude to Messrs. Macmillan for their public-spirited expenditure upon a work which can scarcely hope for a wide circulation in these early days of the growing science of crystall graphy.

Physical Measurements. By A. WILMER DUFF and ARTHUR W. EWELL. Second Edition, Revised and Enlarged. London: J. and A. Churchill. 1911. (7s. 6d.).

IN their "Introduction" the authors point out that the object of a course in laboratory physics is not only the attainment by personal experimentation of a more definite knowledge of the facts and principles of physics, and an acquaintance with the use of measuring instruments and methods, but also the acquisition of a scientific habit of accuracy and carefulness in observing and examining phenomena and drawing conclusions therefrom. The book, written by experienced teachers for the use of advanced students, is a selection of concise clearly written exercises in the methods of performing most of the physical measurement needed in a college course. The subjects dealt with are mechanics, heat, sound, light, and electricity and magnetism. Simple illustrations are given of the essential parts of the various apparatus used, and at the end of each exercise a series of "Questions" is asked involving the principles laid down. At the end of the book there is a large collection of useful tables, including four-figure logarithms. There is also a good index and table of contents.

Institute of Chemistry.—Past List, March-April Examinations, 1911.—Of 13 candidates who presented themselves for the Intermediate Examination, 9 passed—L. E. Campbell, B.Sc. (Lond.); R. B. Croad; A. J. Hale, B.Sc. (Lond.); W. F. Hollely; W. G. Prescott; C. J. Regan, B.Sc. (Lond.); C. B. Roos, B.Sc. (Lond.); H. B. Stevens; and A. F. Suggett. Of 19 candidates who presented themselves for the Final Examination, 12 passed. In the Branch of Mineral Chemistry—W. O. Andrews, A.R.C.S. (Lond.); C. D. V. Georgi, B.Sc. (Lond.); H. L. Lucking, Ph.D. (Heidelberg); and O. D. Roberts. In the Branch of Metallurgical Chemistry—Gordon Wells, B.Sc. (Lond.), A.R.S.M., A.R.C.S. In the Branch of Organic Chemistry—E. de Barry Barnett, B.Sc. (Lond.); G. E. Pool, B.Sc. (Lond.); and G. E. Slim. In the Branch of the Chemistry of Food and Drugs and of Water—S. W. Bridge; A. A. Eldridge, B.Sc. (Lond.); C. H. Hampshire, B.Sc. (Lond.),; and H. M. Mason.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 9, February 27, 1911.

Direct Etherification and Saponification by Catalysis.—Paul Sabatier and A. Mailhe.—Titanic oxide, TiO_2, can be used as a catalyser in etherification, and at temperatures from 280—300° it gives a yield of about 71 per cent of ether from mixtures of equal numbers of molecules of methyl, ethyl, &c., alcohols with acetic acid and its homologues. Thorium oxide is a less satisfactory catalyser in these reactions, but is preferable for the etherification of benzoic and the toluic acids. The ether salts can be directly saponified by water in presence of these catalysing oxides.

Duration of Phosphorescence of Uranyl Salts.—Jean Becquerel.—In the case of a certain number of uranyl salts, principally salts of organic acids, acetates, tartrates, oxalates, &c., their phosphorescence is of decidedly longer duration at low temperatures than at the ordinary temperature. At −193° some of them remain luminous for some seconds after the removal of the tube from the phosphoroscope. Other salts, *e.g.*, the sulphates (simple and complex) and the nitrate of uranyl, show no difference in the duration of the phosphorescence.

Compounds of Amines with Acetylenic Ketones.—Emile André.—The primary and secondary amines can combine with acetylenic ketones of formula $C_6H_5C{\equiv}C{-}CO{-}R$, where R is a cyclic or aliphatic radical. In the case of the primary amines an acetylenic imine of formula $C_6H_5C{\equiv}C{-}C=(N{-}R'){-}R$ seems to be formed as an intermediate product, but these compounds are very unstable and rapidly alter in the air, a second reaction giving the β-substituted ethylenic amines. The secondary amines do not undergo the first reaction but give the β-substitution products directly.

MEETINGS FOR THE WEEK.

MONDAY, 8th.—Royal Institution, 5. General Monthly Meeting.
—— Royal Society of Arts, 8. (Cantor Lecture). "Rock Crystal, its Structure and Uses," by Dr. A. E. H. Tutton.

TUESDAY 9th.—Royal Institution, 3. "The Institute of France," by J. E. C. Bodley.
—— Royal Society of Arts, 4.30. "Canada and Canadian Banking," by F. W. Taylor.

WEDNESDAY, 10th.—Royal Society of Arts, 8. "Beet Sugar Factories," by H. Williams, M.I.Mech.E., &c.

THURSDAY, 11th.—Royal Institution, 3. (The Tyndall Lecture). "The Optical Properties of Metallic Vapours," by Prof. R. W. Wood, LL.D.
—— Royal Society. "Method of Making Visible the Paths of Ionising Particles through a Gas," by C. T. R. Wilson. "Vertical Temperature Distribution in the Atmosphere over England, and some Remarks on the General and Local Circulation," by W. H. Dines. "Mineral Constituents of a Dusty Atmosphere," by W. N. Hartley. "Path of an Electron in Combined Radial Magnetic and Electric Fields," by H. S. Allen. "Absolute Measurement of Light—a Proposal for an Ultimate Light Standard," by R. A. Houston. "Harmonic Expansions," by A. C. Dixon.

FRIDAY 12th.—Royal Institution, 9. "Biology and the Cinematograph," by Prof. W. Stirling, M.D., &c.
—— Physical Society, 8. "Stream Lines Past the Elliptic Cylinder and Magnetic Interpretation," by Sir George Greenhill and Col. R. E. Hippisley. "The Method of Constant Rate of Change of Flux as a Standard for Determining Magnetisation Curves of Iron," by J. T. Morris and T. H. Langford. Demonstration of an Electric Thermo-regulator, by H. L. Callendar.

SATURDAY, 13th.—Royal Institution, 3. "Walter Pater; or the Connoisseur and Art," by Prof. Selwyn Image, M.A.

THE CHEMICAL NEWS.

Vol. CIII., No. 2685.

THE OXIDATION AND AUTO-REDUCTION OF HYDRAZINES.

By F. D. CHATTAWAY, F.R.S.

All chemists who have had occasion to preserve phenylhydrazine know that the reagent, in corked or stoppered bottles, darkens and decomposes with great rapidity, and that even in sealed tubes a small quantity of liquid almost invariably covers the pale yellow crystals.

When kept for any length of time it is no unusual experience to find that the phenylhydrazine has completely disappeared, its place being taken by a mixture of water and benzene coloured reddish brown by small quantities of tarry products.

Phenylhydrazine, when spilt or allowed to run down the side of a bottle, quickly disappears; its characteristic smell vanishes, and only a dark stain due to a minute quantity of some tarry substance remains.

The naphthyl hydrazines, again, which are sometimes sent out in corked bottles, if kept for any length of time before use, are generally found when required to have completely disappeared, only a somewhat discoloured mass of naphthalene being left. Very often, too, glass tubes in which hydrazines are sealed up show some slight pressure when opened, while a strong smell of ammonia as well as of a hydrocarbon or substituted hydrocarbon can be recognised.

Emil Fischer, in his original paper describing the preparation of phenylhydrazine, noted that when it was distilled in large quantity at the ordinary pressure, ammonia, which he removed by exposing the distillate in a vacuum over sulphuric acid, was invariably liberated. He later recognised that this and other hydrazines could not be boiled under ordinary atmospheric pressures without slight decomposition, and recommended that the bases should be distilled under diminished pressure. He states that phenylhydrazine boils between 241° and 242° under a pressure of 750 mm. with the mercury thread entirely in the vapour, but that ammonia is always then liberated, and that the distillate smells strongly of it; under 35 mm. pressure, however, it distils quite undecomposed. Even distillation under diminished pressure was apparently not found sufficient to obtain it in a condition of perfect purity, for later Fischer recommended that after distillation under diminished pressure it should be frequently frozen out from double its volume of ether at about −10°.

This, however, is somewhat tedious, and phenylhydrazine may be obtained in a condition of purity much more easily by distilling it in the partial vacuum obtained by a good water-pump, rejecting the portion coming over before the boiling-point becomes constant. On collecting the distillate in a stoppered bottle, which it should nearly fill, and allowing it to stand in a cool place, the bulk of it crystallises beautifully. The very small quantity remaining iquid should then be poured off, and after re-melting the process should be repeated. After two or three solidifications the compound is pure. Avoiding exposure to the air as far as possible, it should then be sealed up at once in small tubes, which should only be opened immediately before the compound is required.

The behaviour of hydrazines when exposed to the air and when distilled has recently been investigated, and it has been shown that these substances are not only attacked with extreme readiness by free oxygen but also decompose in a characteristic manner when heated. This investigation has cleared up the hitherto unexplained behaviour of these familiar reagents.

Hydrazines when in bulk are oxidised comparatively slowly by free oxygen, as action can only take place at the surface of contact; when, however, this is much increased, as by powdering solid hydrazines or exposing liquid hydrazines in thin films, oxidation takes place rapidly, sometimes with considerable evolution of heat.

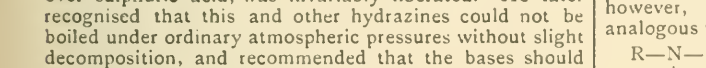
If, for example, sheeets of filter-paper are soaked with phenylhydrazine and placed in large stoppered bottles filled with oxygen, action is very rapid, the bottles quickly become warm from the heat evolved, and a dew collects upon the sides. The liquid covering the paper, at first pale yellow, becomes stained reddish brown, and this colour deepens as time goes on. After being kept at the ordinary temperature for about a week the oxygen is found to have disappeared completely, its place being taken by a greater volume of nitrogen. If sufficient oxygen is present to oxidise the hydrazine completely, benzene, nitrogen, and water are the sole products, disregarding the very small amount of tarry matter formed. All other aromatic hydrazines behave similarly.

This oxidation accounts for the apparent disappearance of phenylhydrazine when spilled and for the odour of hydrocarbon (or hydrocarbon derivative in the case of substituted hydrazines) which is noticed when a compound of this nature is kept in a loosely stoppered bottle. The naphthyl hydrazines, for example, when thus kept appear to become transformed into a somewhat discoloured mass of naphthalene, the water and nitrogen produced escaping unnoticed.

The reactions which occur when hydrazines are oxidised are general ones. For example, oxidation takes a precisely similar course with every aromatic hydrazine of the general formula $RHN \cdot NH_2$, oxygen is absorbed, nitrogen is liberated, and the $—RHNH_2$ group is replaced by hydrogen, thus:—

$$2RHN—NH_2 + O_2 = 2RH + 2N_2 + 2H_2O.$$

This process can be simply formulated by assuming that when a primary aromatic hydrazine is oxidised the hydrogen of the $—NH_2$ group is first attacked and a hydroxy hydrazine produced. Such a molecular structure, however, not being stable, undergoes a disruption, analogous to the typical diazonium decomposition, thus:—



Potassium hydroxide, and to a less extent sodium hydroxide, very much accelerate the rate at which such hydrazines are oxidised. In some cases, as, for example, with phenyl hydrazine, the rate is so much increased that, on merely exposing a solution of the hydrazine in alcoholic potash for a short time to the air, the temperature rises and nitrogen is given off so rapidly that the liquid effervesces vigorously.

Primary aromatic hydrazines are also readily attacked by most substances capable of giving up oxygen at all easily, the products being in the main the same as when free oxygen is used.

Potassium chromate is the most suitable agent to employ. This compound in alkaline solution oxidises all primary aromatic hydrazines very easily, giving a practically theoretical yield of nitrogen and hydrocarbon, and being itself reduced to potassium and chromium hydroxides. The oxidation is most conveniently carried out by dissolving one and a-half times the amount of potassium chromate needed and an equal weight of potassium hydroxide in about ten times its weight of water, adding the hydrazine and blowing steam into the mixture. The action progresses quietly, the nitrogen escapes, the hydrocarbon condenses with the steam, and hydrated chromium hydroxide separates from the liquid. The nitrogen is liberated quantitatively, and in a carefully conducted experiment a practically theoretical yield of hydrocarbon can be obtained.

This reaction is most suitable for estimating the amount of any primary aromatic hydrazine, the nitrogen evolved being collected and measured.

It also affords the most satisfactory method yet described of replacing an amino-group by hydrogen, the former being converted through the diazonium salt into the hydrazino-group and the latter oxidised to hydrogen as described.

The action which takes place when any primary aromatic hydrazine of the formula $RHN.NH_2$ is heated is also a characteristic general one. Auto-reduction occurs, one molecule reducing another, and being itself oxidised, thus:—

$$2RHN.NH_2 = R.NH_2 + NH_3 + N_2 + RH.$$

For example, phenylhydrazine when heated under ordinary atmospheric pressure to its boiling-point, 241—242°, decomposes comparatively rapidly, and it is this auto-reduction which gives rise to the ammonia always noticed when it is thus distilled. About twelve hours' heating at this temperature is sufficient to decompose quantitatively any given amount of phenylhydrazine into aniline, benzene, ammonia, and nitrogen.

This auto-reduction of phenylhydrazine takes place completely and at once if its vapour is passed through a short length of hard glass tubing packed with porous porcelain and heated to dull redness.

Other hydrazines behave similarly, and most are thus decomposed when heated much more rapidly than phenylhydrazine.

Auto-reduction takes place slowly at the ordinary temperature, and the slow decomposition which hydrazines undergo on keeping, even when air is excluded, is due to this.

It is thus impossible to obtain any hydrazine in a state of perfect purity by distillation, or to retain it in this condition for any considerable length of time.

University Chemical Laboratory, Oxford.

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.*

First Paper.—The Analysis of Neodymium Chloride.

By GREGORY PAUL BAXTER and HAROLD C. CHAPIN.

(Continued from p. 111).

The Method of Analysis.

In order to dissolve the chloride the boat was first transferred to a large dry Erlenmeyer flask, a column of bulbs was inserted in the neck of the flask, and enough water to cover the boat was introduced through the bulbs. These precautions were taken because of the violence of the action of the water upon the finely divided anhydrous salt, in order to avoid both mechanical loss of material and possible evaporation of hydrochloric acid, owing to hydrolysis at the high temperature which results at the moment when the salt comes in contact with water. That the error is not a serious one is evident from the fact that although in the first five analyses the use of the column of bulbs was omitted, yet the results of these analyses are not markedly different from the others. The solution was allowed to stand in the flask for some time in order to ensure absorption of any volatilised hydrochloric acid. Every specimen of salt dried and dissolved in this way gave a perfectly clear solution.

The solution of the neodymium chloride was diluted to a volume of about 1 litre with water containing a small amount of nitric acid. Then an equally dilute solution of a very nearly equivalent amount of pure silver nitrate containing nitric acid was added to the solution of the chloride. The glass stoppered precipitating flask containing the solution was thoroughly shaken and allowed to stand for about twenty-four hours, and then an excess of silver nitrate of about one-tenth of a grm. was added to complete the precipitation.

After standing until the supernatant liquid was perfectly clear, the precipitate was thoroughly washed, first with dilute silver nitrate solution and then with very dilute nitric acid in the earlier analyses, with pure water in the later ones, and was collected upon a weighed Gooch-Munroe-Neubauer crucible. Then, after the crucible and contents had been dried in an electric air-bath at about 150° for eighteen hours, they were weighed.

The moisture retained by the dried silver chloride was estimated in each analysis by determining the loss in weight during the fusion of the dried silver chloride in a weighed porcelain crucible. The weight of silver chloride dissolved in the filtrate and silver nitrate wash-waters was assumed to be 0·00003 grm. per litre (Richard and Wells, *Pub. Carnegie Inst.*, 1905, No. 28, 30; *Journ. Am. Chem. Soc.*, xxvii., 487). That dissolved in the acid or aqueous washing together with the ammonia rinsings of the precipitating flask was determined by comparison with standard solutions in a nephelometer, the usual precautions being taken to secure uniformity of precipitation (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235; 1906, xxxv., 510; Richards and Stähler, *Pub. Carnegie Inst.*, 1907, No. 69, 20; *Journ. Am. Chem. Soc.*, xxix., 635).

When the ratio of the neodymium chloride to metallic silver was to be determined, a quantity of silver equivalent to the chloride within a very few tenths of a mgrm. was weighed out and dissolved in nitric acid in a flask fitted with a column of bulbs to prevent loss of material by spattering. The quantity of silver was adjusted exactly by means of a hundredth normal solution of silver. After the silver solution had been freed from oxides of nitrogen it was diluted to a volume of 1 litre, and was quantitatively added to the chloride solution. The precipitate was caused to settle completely by occasional shaking, and standing for several days. Then portions of the mother-liquor were tested for excess of silver or chloride by the addition of hundredth normal chloride or silver nitrate solutions, and comparison of the opalescence produced in a nephelometer. Deficiencies in either chloride or silver were made up by means of the dilute standard solutions of these substances until finally exactly equivalent amounts of chloride and silver were present in the solution.

In all except the first two titrations the solubility of the silver chloride in the mother-liquor was very much decreased by cooling the solution with ice-water, a method of increasing the accuracy of nephelometric observation which has been devised recently by Richards and Willard, and used successfully in their revision of the atomic weight of lithium (*Pub. Carnegie Inst.*, 1910, No. 125, 30; *Journ. Am. Chem. Soc.*, xxxii., 32).

As soon as equilibrium had been reached in a titration, an excess of one-tenth of a grm. of silver nitrate was added, and the silver chloride was determined gravimetrically as described above. Corrections were, of course, applied for any chloride added in the titration.

The Determination of the Moisture Retained by the Neodymium Chloride.

Although in several cases where hydrated salts have been dried by efflorescence it has been shown that the moisture retained by the salt is negligible in quantity (Baxter and Coffin, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1587; Baxter and Tilley, *Ibid.*, 1901, xxxi., 212), in the present instance careful experiments were instituted to test this point thoroughly. The direct determination of the water by absorption with phosphorus pentoxide, after fusion of the salt, was complicated in the case of neodymium chloride, since, if the salt is fused in nitrogen, after being dried, hydrochloric acid is liberated, owing to hydrolysis with the residual moisture. Fusion in a current of hydrochloric acid gas is not permissible because of the action of this gas upon the phosphorus pentoxide necessary for the absorption of the water (Baxter and Hines, *Journ. Am. Chem. Soc.*, 1906, xxviii., 779).

Fortunately, neodymium chloride is only very slightly volatile at temperatures not far above its fusing-point, so that it is possible to estimate the moisture content of the dried salt by fusion in a current of hydrochloric acid gas

* *Journal of the American Chemical Society*, xxxiii., No. 1.

and determination of the loss in weight. (Neodymium chloride fuses at 785°, and is not volatile at 1000° according to Matignon *Comptes Rendus*, 1901, cxxxiii., 289; 1905. cxl., 1340). The trace of chloride volatilised during the fusing can then be collected and weighed.

For these experiments a glass tube is obviously unsuited owing to the action of the hydrochloric acid upon the glass at the fusing-point of the chloride, and consequent vaporisation of alkali chloride into the neodymium chloride as well as into the cooler parts of the tube. Hence in these experiments a quartz tube was substituted for glass. This tube was apparently not attacked by the hydrochloric acid gas during a long series of experiments.

The exact procedure was as follows:—The boat with a maximum charge of neodymium chloride crystals was heated in a current of nitrogen and hydrochloric acid gases, and was bottled and weighed exactly as in preparing the salt for the chloride analyses. After being weighed the boat was replaced in the quartz tube, and when the air had been completely displaced by hydrochloric acid gas, the tube was electrically heated by means of a removable mica sleeve wound with the resistance wire "nichrome," until the salt was fused. The boat was then bottled in dry air a second time, and re-weighed. In nearly every experiment a barely visible condensation of concentrated hydrochloric acid solution took glace in the cool portion beyond the boat.

Weight of $NdCl_3$. Grms.	Loss in weight during fusion. Grm.	Percentage loss in weight.
5·36	0·00045	0·0084
6·73	0·00052	0·0077
5·93	0·00050	0·0084
	Average	0·0082

The loss in weight of the salt found in this way is caused in part by a slight sublimation during the fusion, the magnitude of which was not determined in the first series of experiments. Since the neodymium chloride employed in the moisture determinations was not of so high a grade of purity as that used in the chloride analyses, the volatilised material probably consisted in part of other chlorides. Hence the proportion of moisture calculated from the loss in weight is certainly a maximum. In a second series of experiments, after the fusion of the salt, the sublimate in the quartz tube was dissolved in water, and the solution evaporated to dryness in the weighed platinum boat, and after drying at 135° in hydrochloric acid gas the boat was re-weighed. (The moisture retained by neodymium chloride at this temperature is only 7·5 per cent of its weight. A higher temperature was avoided in order that no portion of the residue might volatilise). The weights thus obtained were subtracted from the loss in weight of the salt found in the same experiment. When the quartz tube was heated alone in hydrochloric acid gas, no sublimate was formed, showing that the volatilised substance did not come from the quartz.

Weight of $NdCl_3$. Grms.	Loss in weight during fusion. Grm.	Weight of volatile matter. Grm.	Per cent of moisture.
6·24	0·00050	0·00030	0·0032
7·19	0·00052	0·00030	0·0031
		Average	0·0032

It is to be noted that the percentage loss in weight in the second series of experiments is identical with that of the first series, although the per cent of moisture is less than half the percentage loss in weight during fusion. The effect upon the atomic weight of neodymium of correcting for the moisture is to lower the atomic weight by eight thousandths of a unit.

The percentage of moisture found is nearly identica in magnitude with that obtained from iodine pentoxide which had been made by efflorescence of iodic acid, 0·0023 (Baxter and Tilley, *Journ. Am. Chem. Soc.*, 1909, xxxi., 212).

The fused neodymium chloride seemed to be perfectly soluble in water, the probable reason for the better success in these experiments than in the earlier ones being the more efficient drying of the salt before fusion.

The Specific Gravity of Neodymium Chloride.

Although Matignon (*Comptes Rendus*, 1905, cxl., 1340) had already found the density of anhydrous fused neodymium chloride at 18° referred to water at 4° to be 4·195, for the purpose of confirmation this constant was re-determined by displacement of toluene. On account of the difficulty of removing air from porous material the salt was fused for these determinations. The pycnometer employed was one of special form, modified by Baxter and Hines (*Journ. Am. Chem. Soc.*, 1904, xxxi., 222).

The salt was first carefully dried, and then finally fused in a current of hydrochloric acid gas in a small platinum boat, as previously described. The boat and contents were then weighed in a small weighing bottle to which they were transferred by means of the bottling apparatus. The salt was next quickly covered with dry toluene, and a special pycnometer stopper was substituted for the ordinary stopper of the weighing bottle. Entangled air was removed by exhaustion in a desiccator, and finally the toluene was adjusted to a mark in a capillary outlet tube in the usual way, after the temperature of the system had been carefully adjusted to 25°. In order to avoid evaporation of the toluene through the ground joint of the pycnometer, this was made tight by means of a weighed quantity of syrupy phosphoric acid. The toluene content of the system being known, the displaced toluene could be found. The specific gravity of the toluene at 25° referred to water at 4° was determined in the same pycnometer to be 0·8636, while Jones in earlier experiments with a different pycnometer found the specific gravity of the same sample to be 0·8633 (Baxter and Jones, *Proc. Am. Acad.*, 1910, xlv., 155; *Journ. Am. Chem. Soc.*, xxxi., 314).

A part of the difference between this value and Matignon's can be explained by the different temperatures at which the determinations were made.

Weight of $NdCl_3$ in vacuum. Grms.	Weight of toluene displaced in vacuum. Grm.	Specific gravity of $NdCl_3$ 25°/4°.
1·9967	0·4177	4·128
3·6878	0·7700	4·136
3·2569	0·6798	4·137
	Average	4·134

If the weights are assumed to have the specific gravity at 8·3 (Baxter, *Proc. Am. Acad.*, 1906, xlii., 209), Matignon's value for the density leads to a vacuum correction per grm. of substance of +0·000141, while the value 4·13 necessitates a correction of +0·000145. The difference amounts to only four ten thousandths of a per cent, which corresponds to a difference of only one thousandth of a unit in the atomic weight of neodymium. Hence it is of no importance which correction is employed.

The following table indicates the corrections for the buoyant effect of the air applied to the weights of the various substances.

	Specific gravity.	Vacuum correction.
Weights	8·3	
Toluene	0·863	+0·00126
$NdCl_3$	4·134	+0·000145
AgCl..	5·56	+0·000071
Ag	10·49	−0·000031

All weighings were made on a nearly new balance, Troemner No. 10, which is employed exclusively in atomic weight researches. Weighings were made by substitution for counterpoises as nearly as possible like the objects weighed both in weight and in volume. The weights were carefully standardised to hundredths of a mgrm. by the method described by Richards (*Journ. Am. Chem. Soc.*, 1900, xxii., 144).

(To be continued).

ANALYSIS OF CRUDE GLYCERIN.

Introductory Note.

A General Meeting of makers of crude glycerin was held in London on July 26th, 1909, at which the following resolution was passed:—

"That in the opinion of this meeting it is desirable for the purposes of the standardisation of the tests of crude glycerin in this country to appoint a Committee to carry out the details."

The Executive Committee appointed by that meeting considered the best methods of procedure, and appointed a Committee of Experts to make investigations and report. The work entailed has been much greater than was ever anticipated.

Committees in other countries have been simultaneously making independent investigations, and it was fortunately found possible to hold joint conferences which have resulted in a general agreement of methods and details.

The Executive Committees desire to acknowledge the voluntary services of the various gentlemen on the Committee of Experts, and the very valuable assistance they have rendered in connection with the subject under investigation.

The working expenses of the Committees (including travelling expenses of those members attending conferences in other countries) have been guaranteed by voluntary contributions from the various companies and firms interested in the subject.

The Executive Committee fully endorses the report herewith submitted.

On behalf of the British Executive Committee.

(Signed) W. Winwood Gossage, Chairman.
Jno. Gray, Hon. Secretary.

Report.

International Standard Methods, 1911.

The valuation of crude glycerin has in recent years assumed greater commercial importance owing to the increased value of the commodity. The want of uniformity in the methods and processes of analyses, together with the irregularity of the results obtained, emphasised the desirability for the standardisation of crude glycerin analysis, so, with this object in view, Committees were formed in America, France, Germany, and Great Britain. These Committees worked, in the first instance, independently; but were ultimately brought together, and after a series of conferences the conclusions arrived at by the various Committees were summarised and drawn up in the form in which they are now presented. The methods detailed in this Report have the unanimous support of each of the above Committees, and are strongly recommended by them as International Standards.

Producers, consumers, and analysts were represented on the Committees. It is hoped that the conclusions arrived at will be found acceptable by all parties interested.

Methods of Crude Glycerin Analysis.
(Recommended by the International Committees).

Sampling.

The most satisfactory method available for sampling crude glycerin liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerin sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (Appendix 1), then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerin. Each drum must be sampled. Glycerin which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerin to be taken, including any deposit.

Analysis.

1. *Determination of Free Caustic Alkali.*—Weigh 20 grms. of the sample into a 100 cc. flask, dilute with approximately 50 cc. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 cc. of phenolphthalein solution, make up to the mark, and mix. Allow the precipitate to settle, draw off 50 cc. of the clear liquid, and titrate with normal acid (N/1). Calculate to percentage of Na_2O existing as caustic alkali.

2. *Determination of Ash and Total Alkalinity.*—Weigh 2 to 5 grms. of the sample in a platinum dish, burn off the glycerin over a luminous Argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilisation and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash, and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash. Dissolve the ash in distilled water, and titrate total alkalinity, using as indicator methyl-orange cold or litmus boiling.

3. *Determination of Alkali present as Carbonate.*—Take 10 grms. of the sample, dilute with 50 cc. distilled water, add sufficient N/1 acid to neutralise the total alkali found at (2), boil under a reflux condenser for fifteen to twenty minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and titrate back with N 1 NaOH using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_2O found in (1). The difference is the percentage of Na_2O existing as carbonate.

4. *Alkali combined with Organic Acids.*—The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

5. *Determination of Acidity.*—Take 10 grms. of the sample, dilute with 50 cc. of distilled water free from carbon dioxide, and titrate with N/1 NaOH and phenolphthalein. Express in terms of Na_2O required to neutralise 100 grms.

6. *Determination of Total Residue at 160° C.*—For this determination the crude glycerin should be slightly alkaline with Na_2CO_3 not exceeding the equivalent of 0·2 per cent Na_2O, in order to prevent loss of organic acids. To avoid formation of polyglycerols this alkalinity must not be exceeded.

Preparation of Glycerin.—Ten grms. of the sample is weighed into a 100 cc. flask diluted with water, and the calculated quantity of N/1 HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 cc., the contents mixed, and 10 cc. measured into a weighed Petri or similar dish 2·5 in. diameter and 0·5 in. deep, which should have a flat bottom. In the case of crude glycerins abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 mgrms.

Evaporation of the Glycerin.—The dish is placed on a water-bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 in. cube, having an iron plate ¾ in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half-way up the oven. On these strips the dish containing the glycerin is placed. If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially open, and the glycerin, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and

allowed to cool. An addition of 0·5 to 1 cc. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C., it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually two to three hours is required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, &c., is repeated until a constant loss of 1 to 1·5 mgrms. per hour is obtained.

Corrections to be Applied to the Weight of the Total Residue.—In the case of acid glycerin a correction must be made for the alkali added. One cc. N 1 alkali represents an addition of 0·022 grm. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight, multiplied by 100, gives the percentage of *total residue at* 160° C. Preserve the total residue for the determination of the non-volatile acetylisable impurities.

7. *Organic Residue.*—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (*Note.*—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition, and that the CO_3 radicle thus derived is not included in the organic residue).

8. *Moisture.*—This test is based on the fact that glycerin can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride. Two to 3 grms. of very pure bulky asbestos freed from acid soluble material which has been previously dried in a water-oven, is placed in a small stoppered weighing bottle of about 15 cc. capacity. The weighing bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 1·5 grms. of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken, and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° C., the weight is constant in about forty-eight hours. At lower temperatures the test is prolonged. The sulphuric acid in the desiccator must be frequently renewed.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 6th, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

"*A Chemically-active Modification of Nitrogen produced by the Electric Discharge.*" (The Bakerian Lecture). By Prof. the Hon. R. J. Strutt, F.R.S.

The leading facts established are :—

1. That pure nitrogen, from whatever source, subjected at a low pressure to the jar discharge, undergoes some modification which causes it to glow for a short time after it has been sucked away from the discharge.

2. The glow which is emitted while the gas returns to its normal condition is not destroyed by the removal of ons. It is weakened by heating, intensified by cooling. This seems to favour the view that it is due to the re-combination of dissociated atoms.

3. The modified nitrogen acts on ordinary phosphorus, combining with it, and at the same time forming much red phosphorus.

4. It combines with sodium and also with mercury at a gentle heat (say, 150° C.), forming in the latter case an explosive compound, and in each case developing the line spectrum of the metal concerned. It also develops the line spectra of other metals, probably combining with them.

5. It develops the band spectra of compounds, when these are vapourised in it, giving in many cases spectra of substances too unstable to be examined at the temperature of the Bunsen flame.

6. It attacks acetylene, and substances like ethyl iodide or chloroform, setting the halogen free when there is one, and combining with the carbon to form cyanogen. This is proved by the brilliant cyanogen spectrum produced, and by direct chemical tests, such as formation of Prussian blue.

7. It attacks nitric oxide, with formation, strangely enough, of nitrogen peroxide, a more oxidised substance.

Papers were read as follows :—

"*Association of Lead with Uranium in Rock-minerals, and its Application to the Measurement of Geological Time.*" By A. Holmes.

"*Dynamical Value of the Molecular Systems which emit Spectra of the Banded Type.*" By Prof. E. T. Whittaker, Sc.D., F.R.S.

It is now widely believed that when the spectrum emitted by a luminous body is of the banded type, the small vibrators which give rise to the radiation are the molecules of the substance, as distinguished from atoms or ions. This result is applied in the main body of the paper, in order to suggest a dynamical system, which is formed of two members in the same way as a diatomic molecule may be supposed to be formed of two atoms, and which has free periods of vibration related to each other by the same formula as holds in the case of banded spectra. This formula presents a certain peculiarity, in that the frequency of vibration occurs in it linearly ; whereas in the equation for determining the free periods of dynamical systems in general, the frequency enters by its square. It is shown that from this peculiarity in the radiation of a molecule certain inferences may be drawn regarding the dynamical character of the connection between the atoms within the molecule. It is shown that a somewhat modified mecnanism would emit radiations connected by the same law as that which Balmer found for the hydrogen lines.

CHEMICAL SOCIETY.

Ordinary Meeting, April 6th, 1911.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 215).

"92. "*A Synthesis of Phenanthrene.*" By James Kenner and Emily Gertrude Turner.

Jackson and White (*Am. Chem. Journ.*, 1880, ii., 383) showed that dihydrophenanthrene is one of the products of the interaction of sodium with *o*-bromobenzyl bromide. The authors are investigating the intermediate products of this reaction with the view of determining from which of them the phenanthrene synthesis is effected.

From *ωω'*-dibromo-2 : 2'-ditolyl, a possible intermediate product, dihydrophenanthrene has been prepared, together with a hydrocarbon, melting at 212—213°, the nature of which has not yet been determined. From *ωωω'ω'*-tetrabromo-2 : 2'-ditolyl a 67 per cent yield of phenanthrene has been obtained.

ωω'-Dibromo-2 : 2'-ditolyl, $CH_2Br{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CH_2Br$, rhombic prisms, m. p. 88°, and *ωωω'ω'-tetrabromo-2 : 2'-ditolyl*, $CHBr_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CHBr_2$, rhombic prisms, m. p. 138°, are formed by bromination of 2 : 2'-ditoyl at 110°.

2 : 2'-Diphenylenediformaldehyde, $CHO{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CHO$,

thin plates, m. p. 62–63° (*hydrazone*, rectangular plates, m. p. 102° with decomposition), was prepared by the hydrolysis of tetrabromoditolyl in dilute alcoholic solution with potassium oxalate. Preliminary experiments have shown that it undergoes condensation when boiled with potassium cyanide, but the product does not yield phenanthraquinone on oxidation.

From the dibromide, 2 : 2'-*diphenylenediacetonitrile*, $CN\cdot CH_2\cdot C_6H_4\cdot C_6H_4\cdot CH_2\cdot CN$, rectangular plates, m. p. 77°, the *diamide*, $NH_2\cdot CO\cdot CH_2\cdot C_6H_4\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH_2$, melting-point 206°, and the *dicarboxylic acid*, $CO_2H\cdot CH_2\cdot C_6H_4\cdot C_6H_4\cdot CH_2\cdot CO_2H$, needles, m. p. 168°, have also been prepared in connection with these studies on cyclic condensation.

93. "*The Correlation of Viscosity with other Physical Properties.* Part I. *The Ethenoid and Ethinoid Unsaturation.*" By Thomas Percy Hilditch and Albert Ernest Dunstan.

The authors intend in this series of papers to compare the viscosity coefficients of a variety of compounds with their molecular refractivity and dispersive power, molecular volume, magnetic rotatory power, optical activity, and other constitutive properties, with the aim of collating a mass of experimental evidence bearing on the general problem of chemical constitution and physical properties.

They propose to obtain comparable viscosity data in two ways :—

(*a*) The quantity $\frac{\eta \times 10^6}{\text{Mol. vol}}$ has been shown to be approximately constant for any given series.

(*b*) The viscosity of solutions of fixed molecular concentration gives a sufficiently exact value for comparative purposes when an appropriate solvent is used.

Seven different series of compounds containing the ethenoid and ethinoid linkings have been studied, and it has been found that, in general, the ethinoid linking produces a greater exaltation in a number of physical properties than the ethenoid. When, however, the unsaturated grouping is conjugated with another nucleus possessing considerable residual affinity (C_6H_5-, CO_2H-,), then the ethenoid anomaly approaches that of the ethinoid.

94. "*Chemical Action induced by Cathode Rays and Canal Rays.*" By Edgar Philip Perman.

The transmutation of copper, thorium, and uranium by means of cathode rays and canal rays has been attempted, and the chemical effect of canal rays on a number of substances has been studied. The following are the chief conclusions :—

(*a*) Neither cathode rays nor canal rays produce any transmutation of the elements.

(*b*) Canal rays in air or oxygen have a strong oxidising action.

(*c*) The oxidising action appears to be mostly direct, but is accompanied by a scattering effect.

(*d*) Many substances are decomposed by the action of canal rays independently of the nature of the gas in which the rays are produced.

95. "*Compounds of Copper Benzoate with Pyridine and Quinoline.*" By Oscar Lisle Brady.

While attempting to acetylate a compound contaminated with copper powder, by means of benzoyl chloride and glacial acetic acid in pyridine solution, a quantity of blue crystalline material was obtained. This was found to contain copper, and on decomposition with alkali hydroxide or acids, pyridine and benzoic acid were formed.

Further experiment showed that the substance may be prepared directly from copper benzoate and pyridine.

Copper benzoate was dissolved in boiling pyridine, and the deep blue liquid allowed to cool. The blue crystalline material which separated was collected and washed with ether.

Found : C = 58·5 ; H = 5·9.

$Cu(C_7H_5O_2)_2,2C_5H_5N,2H_2O$ requires C = 57·6 ; H = 4·8 per cent.

On heating in the steam-oven, the compound lost 20·3 per cent of its weight, yielding a bright green substance, which contained C = 57·4 ; H = 4·8 ; CuO = 19·0.

$Cu(C_7H_5O_2)_2,2C_5H_5N,2H_2O$ loses 19·5 per cent of its weight to give $Cu(C_7H_5O_2),C_5H_5N,H_2O$, which requires C = 56·6 ; H = 4·2 ; CuO = 19·6 per cent.

The loss in weight on heating, and the percentage of carbon and hydrogen being high, whilst the value for copper oxide is low, may be accounted for by the presence of free pyridine, as both compounds have a strong odour of the base.

Similar results were obtained when quinoline was substituted for pyridine, but the blue compound was less stable, washing with ether being enough to remove quinoline with the formation of a green substance.

The blue quinoline compound was found to contain C = 70·5 ; H = 5·8 ; and the green compound obtained from it by heating in the steam-oven gave C = 61·7 ; H = 4·2 ; CuO = 18·0 :—

$Cu(C_7H_5O_2)_2,4C_9H_7N,2H_2O$ requires C = 69·9 ; H = 4·9 per cent.

$Cu(C_7H_5O_2)_2,C_9H_7N,H_2O$ requires C = 61·4 ; H = 4·2 ; CuO = 17·5 per cent.

96. "*Experiments on the Synthesis of the Terpenes.* Part XVIII. *Synthesis of* Δ^5*-o-Menthenol*(8), Δ^6*-o-Menthenol*(8), *and the Corresponding Menthadienes.*" By William Henry Perkin, jun.

The *cis*- and *trans*-1-methyl*cyclo*hexan-6-ol-2-carboxylic acids, which are produced by the reduction of 6-hydroxy-*o*-toluic acid, are converted into the corresponding 6-bromo-derivatives, and the esters of these, when digested with diethylaniline, give rise to a mixture of *ethyl 1-methyl-*Δ^5- and 1-*methyl-*Δ^6-cyclo*hexenecarboxylates*.

These are separated by fractional esterification and hydrolysis, and are converted, by means of magnesium methyl iodide, into the corresponding menthenols, from which the corresponding menthadienes are obtained by shaking with cold 5 per cent sulphuric acid or by boiling with 6 per cent oxalic acid.

97. "*Experiments on the Synthesis of the Terpenes.* Part XIX. *Synthesis of* cis- *and* trans-Δ^3*-o-Menthenol*(8), Δ^4*-o-Menthenol*(8), *and the corresponding Menthadienes.*" By William Henry Perkin, jun.

By the same series of reactions as described in the preceding paper, 4-hydroxy-*o*-toluic acid is converted into cis- and trans-Δ^3-*o-menthenol*(8) and Δ^4-*o-menthenol*(8), which yield the corresponding *menthadienes*.

98. "*The Condensation of Ethyl Crotonate and Ethyl Methylacrylate with Ethyl Cyanoacetate and Ethyl Bromoacetate. Synthesis of* γ*-Methylbutane-*$\alpha\beta\delta$*-tricarboxylic Acid and Pentane-*$\alpha\beta\delta$*-tricarboxylic Acid.*" By Edward Hope and William Henry Perkin, jun.

When ethyl crotonate is condensed with ethyl sodiocyanoacctate and the product treated with ethyl bromoacetate, ethyl β-cyano-γ-methylbutane-$\alpha\beta\delta$-tricarboxylate is obtained. On hydrolysis and elimination of carbon dioxide, this yields γ-methylbutane-$\alpha\beta\delta$-tricarboxylic acid.

By a similar series of reactions pentane-$\alpha\beta\delta$-tricarboxylic acid is prepared from ethyl methylacrylate and ethyl sodiocyanoacetate. These acids form the starting point for the preparation of *cyclo*pentanonecarboxylic acids.

99. "*The Volume of a Solute in Solution.* Part II. *The Influences of Molecular Association, Solvate Formation, and Ionisation.*" By Dan Tyrer.

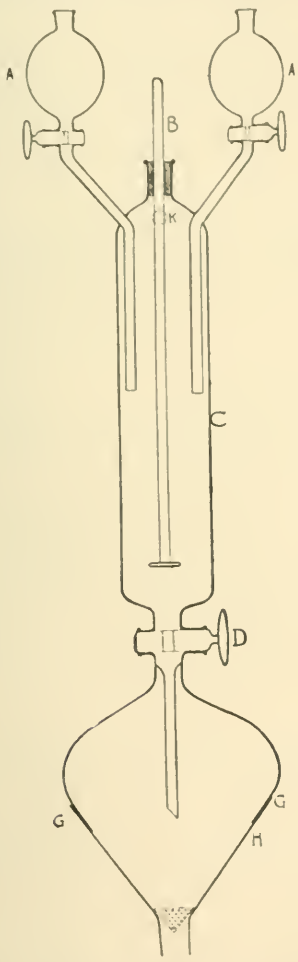
The specific solution volumes of various substances which polymerise in solution have been measured in normal non-associated solvents. It was found that molecular association is quite without influence on the specific solution volume of the solute. Measurements were made also for solutions in which solvates are formed. In these cases it was found that, as a general rule, the specific volume of the solute in solution increased regularly with increase of the concentration. Several exceptions, however, to this rule were observed. In the

case of aqueous solution, the conclusion was drawn that hydrates exist in the majority of cases, and with strong electrolytes the evidence points to the existence of hydrated ions.

100. "*An Apparatus for Precipitating, Filtering, and Drying in an Inert Gas.*" By James Brierley Firth and James Eckersley Myers.

The apparatus designed for the above purpose is shown in the accompanying sketch.

The reacting liquids are placed in the funnels, A, A, and the remainder of the apparatus is evacuated through a Büchner flask fitted to the filter-funnel H. The apparatus is then filled with the inert gas through a side-tube at K. The tap D being closed, the reacting liquids are run into the precipitating tube C, and are mixed by means of the stirrer B, which slides in a rubber stopper lubricated with



rubber grease. When the reaction is complete, the tap D, which has a wide bore, is opened, and the precipitate filtered off in the funnel H. The washing and drying are carried out by drawing suitable liquids through the precipitate, and finally aspirating a stream of the inert gas to remove the liquids used for drying. There is a ground glass joint at G, by means of which the funnel is prepared for filtration and the precipitate is removed. This apparatus is being used with satisfactory results in the preparation of copper hydride.

(We are indebted to the Chemical Society for permission to reproduce the accompanying illustration).

101. "*Triketohydrindene Hydrate.* Part III. *Its Retation to Alloxan.*" By Siegfried Ruhemann.

β-Hydrindone, as well as 1 : 3 diketohydrindene, may be transformed into triketohydrindene hydrate by Sachs-Barschall's method, but they are less suitable for the preparation of this compound than α-hydrindone (see Ruhemann, *Trans.*, 1910, xcvii., 1438). The blue colour reaction which the triketone yields with amino-acids (*Trans.*, 1910, xcvii., 2025) was applied to a large number of these substances, and it was found that the triketone is a valuable reagent for proteins and their hydrolytic products. The coloration is accompanied by the production of aldehydes, which points to a similarity between triketohydrindene hydrate and alloxan. This is indicated, also, by the formation of a compound which closely resembles alloxantin, and which is called *hydrindantin*. In accordance with the formula of alloxantin (Piloty and Finckh, *Annalen*, 1904, cccxxxiii., 68; Slimmer and Stieglitz, *Am. Chem. Journ.*, 1904, xxxi., 661), the constitution of hydrindantin is represented thus :—

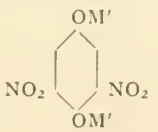
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)\cdot O\cdot CH<\begin{matrix}CO\\CO\end{matrix}>C_6H_4.$$

This substance, like alloxantin, is colourless, crystallises with 2 mols. H_2O, and is very sparingly soluble in water; with amino-acids it gives the same coloration as triketohydrindene hydrate. It forms two different sodium salts, according as to whether sodium carbonate or sodium hydroxide is used; one is a dark red salt, and the other is deep blue. With baryta, it yields a blue barium compound, like alloxantin. These salts are decolorised by oxygen. The colourless alkaline solution which is thus formed from hydrindantin contains *o*-carboxymandelic acid. The constitution of these chromo-salts was discussed, and an account was given of the results of the physiological examination of triketohydrindene hydrate.

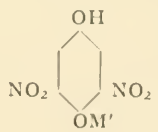
102. "*Salts of 3 : 5-Dinitroquinol.*" By William Bayliss Shaw.

It has been found possible to obtain a complete series of the alkali metal salts of 3 : 5-dinitroquinol by adding an alcoholic solution of the metallic hydroxide to an ethereal solution of the free nitro-compound.

The neutral salts (I.) are in every case darker in colour than the acid salts (II.), and the colour deepens progressively from lithium to cæsium as the atomic weights of the metals increase.



I.



II.

The known barium salts have also been investigated, but their properties have not been found to agree with the descriptions given in the literature.

Evidence has been found to support the view that dinitroquinol contains the nitro-groups in the meta-position to one another, and not in the para-position as assumed by Beilstein.

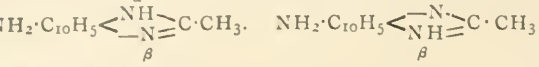
By acting on dinitroquinol with methyl sulphate under suitable conditions the monomethyl ether can be obtained, but the formation of the dimethyl ether by this means does not seem to be possible.

The alkali metal salts of the monomethyl ether have been prepared and investigated.

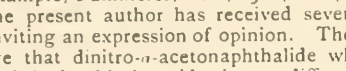
103. "*The Question of Isomerism between Naphthiminazoles.*" By Raphael Meldola.

In a series of papers communicated to the Society some years ago by the author in collaboration with various students (*Trans.*, 1899, lxxv., 1011; 1900, lxxvii., 1159; 1903, lxxxiii., 1185; 1904, lxxxv., 1592), a pair of amino-

naphthiminazoles and their derivatives were described, which, according to the evidence obtained, were structurally isomeric in the sense indicated by the formulæ :—



If this isomerism really existed, it would have been opposed to the theory of "virtual tautomerism" applied by Otto Fischer to a somewhat parallel case in the benzene series (*Ber.*, 1901, xxxiv., 4202; *Journ. Prakt. Chem.*, 1906, [2], lxxiii., 423 *et seq.*). In view of this conflict of evidence, the subject was reinvestigated by this last-named author, who came to the conclusion that one of the supposed isomerides belonged to the series of oxyiminazoles" first described by St. v. Niementowski (*Journ. Prakt. Chem.*, 1907, [2], lxxv., 88). The subject has frequently been referred to since the publication of Fischer's last paper, and has aroused much interest in view of the importance of the theoretical principle involved (see, for example, Pummerer, *Ber.*, 1911, xliv., 343 and 810), and the present author has received several communications inviting an expression of opinion. The facts briefly stated are that dinitro-α-acetonaphthalide when reduced by tin and hydrochloric acid gives a different compound from that which is obtained when the reduction is effected by means of iron and hydrochloric acid (Markfeldt's process). According to Fischer, the base obtained by the first method is an "oxyanhydro-base" :—



The evidence on which Fischer based this conclusion was mainly derived from the observation that the corresponding naphthiminazole on distillation with iron powder gave the known naphthiminazole (ethenyldiaminonaphthalene) of Prager (*Ber.*, 1885, xviii., 2161). It may be pointed out, as Fischer does not refer to this point, that the author had already recorded the transformation of the aminonaphthiminazole prepared by using tin and hydrochloric acid into Markfeldt's base, by the action of iron and hydrochloric acid (Meldola, Eyre, and Lane, *Trans.*, 1903, lxxxiii., 1200).

As it will be some time before the author can undertake to re-investigate this subject, he desires to place on record the opinion that Fischer's view of the constitution of the compound prepared by using tin and hydrochloric acid is probably correct, although the method of distilling with iron powder must be regarded as a somewhat violent one when the point to be decided is whether the oxygen in a compound is constitutional or whether it is present in the form of attached water. This is, of course, independent of the question of concordant analytical results, which, in the case of these difficultly combustible compounds, are by no means easy to obtain. The attachment of water to anhydro-bases with varying degrees of pertinacity has long been familiar to workers in this field, and it now appears that many of the iminazoles described by the earlier investigators as containing water of constitution and water of crystallisation may really be "oxyiminazoles." St. v. Niementowski is himself continuing the investigation of the latter class of compounds (*Ber.*, 1910, xliii., 3012). The present case is certainly remarkable as an instance of the failure of tin and hydrochloric acid to remove the whole of the oxygen where iron and this acid are effective. The mechanism of this reduction is best explained by the assumption that the hydroxylamine phase is passed through as an intermediate stage :—

This possibility was frequently considered during the progress of the research, and several unsuccessful attempts were made to arrest the reduction at an intermediate stage. The dinitro-α-acetonaphthalide is extremely insoluble in the usual organic solvents, and the reduction has therefore to be carried on at a temperature too high to admit of the isolation of an intermediate compound.

While accepting Fischer's view of the constitution of the one series, the author wishes to point out that it seems desirable to obtain further confirmation of the "oxyiminazole" formula, as there is reason for believing that the oxygen in this ring may be easily eliminated in unforeseen ways in the course of the reactions to which these compounds may be submitted (see St. v. Niementowski, *Ber.*, 1910, xliii., 3016). Some of the author's results published in the papers referred to, and which are apparently opposed to the "oxyiminazole" formula, may perhaps be explained from this point of view. The azo-derivatives of both the anhydro-bases give well-defined products on complete reduction; they also give rise to very remarkable compounds when acted on by nitrous acid, and to other and also apparently definite products when decomposed by alkali (Meldola and Eynon, *Trans.*, 1900, lxxvii., 1167, 1169). The study of these various derivatives may throw further light on the question of the constitution of the parent compounds.

104. "*The Determination of the Density of Liquids.*" By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

The precautions necessary in accurate density determinations involving the use of small quantities of liquid were discussed, and a modified form of pyknometer was described.

105. "*The Influence of Temperature on the Basic Water Value of Ethyl Alcohol.*" By WILLIAM JACOB JONES and ARTHUR LAPWORTH.

The authors discussed in detail the theory of Goldschmidt and Udby which led them to suppose that the carriers of catalytic activity of acids in water and in alcohol are the cations to which the main part of the conductivity of each solution is due.

Measurements were described showing that the basic water value of anhydrous ethyl alcohol varies from about 0·050 at 0° to 0·097 at 25°, the results being nearly the same, whether obtained by determinations of the effect of water on the catalytic activity or on the salt-forming capacity (availability) of dissolved hydrogen chloride.

The heat of the reaction :—

$$C_2H_6O,HCl + H_2O = C_2H_6O + H_2O,HCl,$$

in dilute solution was estimated as, roughly, 1100 grm.-calories.

106. "*Synthesis and Resolution of Gnoscopine* (dl-*Narcotine*." By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

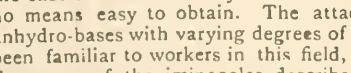
A detailed description was given of the synthesis and resolution of gnoscopine, a preliminary account of which has already appeared (*Proc.*, 1910, xxvi., 46, 131).

107. "*The Occurrence of Alizarin in Rhubarb.*" By HUGO MÜLLER.

The author has continued his investigations on rhubarb, and finds that the root contains alizarin as well as emodin and chrysophanic acid.

108. "*Coumaranone Derivatives.* Part I." By RICHARD WILLIAM MERRIMAN.

Ethyl coumaranonecarboxylate,



the "oxygen" analogue of ethyl indoxylcarboxylate, prepared by internal condensation of ethyl salicylylglycollate (Friedländer, *Ber.*, 1899, xxxii., 1868), is not hydrolysed by alkalis, as stated by that author, but forms various

well-defined metallic derivatives. The *sodium* and *lead* compounds are colourless, the *silver* derivative is yellowish and unstable, and the *ferric* derivative forms very characteristic deep blue nodules, soluble in alcohol and ether, but insoluble in water, light petroleum, or benzene. In acetic acid solution, however, the ester, under certain ill-defined conditions, forms a yellow *hydrazone* (needles, m. p. 125—126°), which is hydrolysed normally by acids or alkalis.

With alcoholic phenylhydrazine the action, although smooth, is altogether abnormal, the first tangible product being an azocompound, which is apparently formed by oxidation of the hydrazide. *Benzeneazocarbonylcoumaranone*, $C_6H_5{\cdot}N{:}N{\cdot}CO{\cdot}CH{<}\begin{smallmatrix}O\\CO\end{smallmatrix}{>}C_6H_4$, forms well-defined orange needles (m. p. 182—183°); it is readily soluble in alkalis, including ammonia, but it is not hydrolysed by them or by acids; the *silver* derivative is a brick-red powder (m. p. 241°, with decomposition). The *hydrazone* of this azo-compound, resulting from the action of excess of phenylhydrazine under the same conditions, forms ruby-red needles (m. p. 193°), and is not acidic.

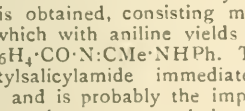
Ethyl o-carboxyphenylglycollate,

$$CO_2Et{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2Et,$$

hitherto known only in an impure state (Rössing, *Ber.*, 1884, xvii., 2995), was readily prepared in quantity for the above work by the direct interaction of ethyl salicylate and ethyl chloroacetate in presence of sodium ethoxide; it is a heavy colourless oil (b. p. 190—193° 25 mm.). In addition to the yellow diamide described by Rössing, it forms a colourless *monoamide* (needles, m. p. 165°).

109. "*The Condensation of Acetyl Chloride and Salicylamide.*" By Arthur Walsh Titherley and William Longton Hicks.

Acetyl chloride and salicylamide interact immediately in the cold, producing the hydrochlorides of salicylamide and N-acetylsalicylamide, the latter evidently by rearrangement of the isomeric *O*-acetyl derivative. By long-continued action of excess of acetyl chloride a white granular solid is obtained, consisting mainly of a chloro-derivative, which with aniline yields *phenylsalicylacetamidine*, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}N{:}CMe{\cdot}NHPh$. The chloro-derivative gives N-acetylsalicylamide immediately on treatment with water, and is probably the impure hydrochloride of the as yet unknown 2-methyl-1:3-benzoxazine-4-one,



, which has resisted all attempts to isolate it.

This unsaturated cyclic compound should, like its phenyl analogue (Titherley, *Trans.*, 1910, xcvii., 204), give a phenylsalicylamidine derivative on treatment with aniline.

The mother-liquor from the above granular solid contains O N-*diacetylsalicylamide*, which, however, is best obtained by pyridine acetylation (using acetic anhydride) of N-acetylsalicylamide. The diacetyl derivative is remarkable in being readily soluble in cold water, and in undergoing slow spontaneous hydrolytic decomposition in air, yielding N-acetylsalicylamide.

110. "*The Influence of Salts on the Autofermentation of Yeast.*" (Preliminary Note). By Arthur Harden and Sydney G. Paine.

It has been found by one of the authors, during an investigation of the permeability of the yeast-cell envelope, that the entrance of such salts as sodium chloride and sodium phosphate is imperceptible when dilute solutions are allowed to act for a short time, and comparatively small even after prolonged immersion of the cells. When, however, more concentrated solutions are employed, an appreciable entrance of the salts is indicated.

These facts, in view of the recent work of H. E. and E. F. Armstrong (*Proc. Roy. Soc.*, 1910, B, lxxxii., 588), therefore suggested the advisability of ascertaining the effect of such salts on the autofermentation of the yeast.

For the experiments here given, top yeast obtained from a London brewery was freed from wort by the simple expedient of pressing, which has been found to give practically quantitative removal of the intersticial liquid; washing was avoided in order that osmotic equilibrium of the cell contents might remain undisturbed.

Three to five grms. of such yeast are accurately weighed out for each experiment, wrapped in tissue paper, and dropped into a flask containing a measured quantity of the liquid under investigation, which has previously been saturated with carbon dioxide at 25°. The gas evolved by autofermentation of the yeast is measured periodically by means of the apparatus described by Harden, Thompson, and Young (*Bio-Chem. Journ.*, 1910, v., 230).

In experiments with sodium chloride and ammonium sulphate it has been found that when these salts are present in decimolar concentration no effect is produced on the autofermentation, but when molar solutions are employed the rate of fermentation is very considerably enhanced during the first four or five hours, so that the volume of carbon dioxide yielded in presence of the salt is three times as great as that given by a water control. At this point, however, the autofermentation in the former case comes abruptly to an end, and eventually after four or five days the volume of gas given in the two cases is approximately the same.

A similar result has also been obtained with a number of other salts, including phosphates, arsenates, acetates, and citrates.

In a recent paper by C. Neuberg and A. Hildesheimer (*Biochem. Zeit.*, 1911, xxxi., 170) it is stated that salts of pyruvic acid are fermentable by yeast, and that this property is also exhibited by salts of glyceric and lactic acids. Similar experiments have been carried out with these salts, and these have shown that the two latter give precisely the same phenomenon as was found in the case of sodium chloride, whilst with potassium pyruvate the rate of fermentation during the first four hours is exactly comparable with that in a sodium chloride control. At this point, however, the fermentation in presence of the latter salt slackens, while the evolution of gas from the pyruvate solution continues and only gradually diminishes. Eventually after four days some 60 cc. of carbon dioxide are yielded in presence of 2·4 grms. of potassium pyruvate in excess of the volume given by the control.

The provisional conclusion of Neuberg and Hildesheimer that these salts undergo fermentation by yeast cannot, therefore, be accepted until experimental proof is forthcoming that the carbon dioxide is actually derived from them, and not from the constituents of the yeast.

The increase in the rate of autofermentation produced by the addition of salts to living yeast may be explicable on the lines suggested by H. E. and E. F. Armstrong, or it may be that, as a result of plasmolysis of the cells, the glycogen is thrown into more intimate contact with the glycogenase.

The acceleration does not appear to be due to a stimulating influence on the glycogenase, since when added to yeast juice in equivalent concentration sodium chloride tends to inhibit, rather than to enhance, the rate of autofermentation.

111. "*Preparation of Secondary Amines from Carboxylic Acids.* Part II. *Preparation of the Heptadecyl and Pentadecyl Derivatives of α- and β-Naphthylamine.*" By Henry Rondel Le Sueur.

The higher alkyl derivatives of both α- and β-naphthylamine are readily obtained by heating the corresponding naphthylamino-acid. Thus, *heptadecyl-α-naphthylamine*, $C_{17}H_{35}{\cdot}NH{\cdot}C_{10}H_7$, and carbon dioxide are produced when *α-1-naphthylaminostearic acid*,

$$C_{16}H_{33}{\cdot}CH(NH{\cdot}C_{10}H_7)CO_2H,$$

is rapidly heated above its melting-point.

PHYSICAL SOCIETY.

Ordinary Meeting, April 28th, 1911.

Prof. H. L. CALLENDAR, F.R.S., President, in the Chair.

A "High-tension Electrostatic Wattmeter" was described by Prof. E. WILSON.

When using the electrometer as a wattmeter it is necessary in (order to secure accuracy) that the voltage impressed upon the quadrants shall not be less than a certain minimum depending upon the voltage to be impressed upon the moving system. When the latter voltage is of the order 10,000, the quadrants require a voltage larger than can economically be provided by a shunt. One is led, therefore, to consider intensifying devices.

The "series" or "current" transformer, whose secondary winding is closed on a non-inductive resistance, can be used to give fairly good results, but it is not accurate at all frequencies and is dependent upon wave form.

The author's quadrature transformer is a very simple piece of apparatus which can be relied upon to give for electrostatic wattmeters an electromotive force which is strictly the differential of the current in the primary winding. When so used it is necessary, for accuracy, at all frequencies and on all wave forms, that the integral of the mains voltage shall be impressed upon the moving system, although for sine curves only the differential need be impressed instead of the integral.

The best device to impress on the quadrants a suitable voltage in phase with the currents is a generator with an air-cored magnetic circuit as described in the paper. The mains current is passed through the field coil of the generator, and produces a magnetic field proportional to the current; the armature is driven at known speed in this field, and is provided with a commutator and brushes. The brushes when set accurately have a voltage between them proportional to, and having the same wave form as, the mains current.

Another device depending upon the charging of condensers in parallel and the placing of them in series has also been used for multiplying a small voltage produced by the passage of the mains current through a low-resistance shunt.

DISCUSSION.

Dr. SUMPNER pointed out that the reason why a fairly high voltage was needed on the quadrants together with a strong control on the needle when a very high voltage was applied to the latter, was because of the action between the needle and the case, unless the case was quite symmetrical about the axis of the needle.

Dr. RUSSELL inquired whether the author was troubled about brush discharges at the edges of the needle.

Mr. E. H. RAYNER pointed out that at low power factors various errors in the apparatus would become large.

Mr. C. C. PATTERSON drew attention to the serious limit of accuracy imposed by not being able to keep the speed constant.

Mr. W. DUDDELL asked if the voltage could not be reduced by means of another quadrature transformer in series with a high resistance, instead of being applied direct to the needle.

Prof. C. H. LEES drew attention to the advisability of reducing the voltage by some means before applying it to the needle.

The AUTHOR, in reply, stated that brush-discharges were fatal to accuracy, but could be detected by observing the apparatus in the dark. Non-inductive high resistances for such voltages as 10,000 or more were very expensive, and he had avoided their necessity.

A paper "*On the Behaviour of Incandescent Lime Cathodes*," by Dr R. S. WILLOWS and Mr. T. PICTON, was read by Dr. WILLOWS.

Wehnelt has shown that incandescent lime emits a large number of negative ions; if therefore hot lime is used as the cathode, a discharge may be obtained in a vacuum tube with P.D. as low as 30 volts. The alteration with time of these cathodes, under continued use, has been investigated, and the following results obtained:—1. When lime is heated on platinum-foil, so far from showing fatigue, it actually increases in activity. With P.D. greater than the saturation voltage this increase may be ninefold. At lower voltages a slow but steady increase up to 100 per cent has been found. The steady activity falls when the lime is cold, the initial activity may greatly increase. 2. When the lime is heated on nickel-foil, if the tube carries a heavy discharge, the current increases to a maximum and then decreases. A greatly increased activity is frequently shown after the lime has been cold for some hours. At the lower voltages the same general variations are shown as with platinum. 3. Great irregularity is frequently shown when the current is first started; at this stage other causes than temperature, such as mechanical vibrations, greatly influence the emission of ions.

DISCUSSION.

Prof. C. H. LEES asked whether the author had examined the film under the microscope. He wanted to know whether there was any likelihood of the film getting detached from the platinum, and also whether the increase of activity was simply dependent upon the quantity of electricity passed.

Dr. WILLOWS, in reply, stated that he had examined the films with a microscope. The films were very adherent to the platinum. It was impossible to render the platinum free again from the activity with which the lime endowed it. There was no connection between the activity and the quantity of electricity passed. The increase of activity was probably due to the CaO diffusing into the platinum.

A paper "*On the Formation of Dust Striations by an Electric Spark*," by Dr. S. MARSH and Mr. W. H. NOTTAGE, was read by Dr. MARSH.

The formation of dust striations by electric spark has been investigated by many observers. The paper attempts to explain their formation as being due to hydrodynamic forces existing between the dust particles while the wave-motion is passing over them. The application of this theory to the striations in a Kundt's tube has been made by Kœnig and Robinson. The wave-motion is assumed to be of the spherical progressive type, and expressions are obtained from the intervals between consecutive striæ and the distances of the striæ from origin. Measurements were made of striæ formed on a glass plate with vertical central spark. The agreement between theory and experiment is within the experimental error. Experiments with channels of various shapes were made. Illustrations of the various striæ patterns obtained with small obstacles and reflecting surfaces are given, and the use of these as a convenient means of indicating reflecting interference and diffraction of sound waves is pointed out.

DISCUSSION.

Mr. A. CAMPBELL thought the authors' results justified their theory. His own experiments had been made with much slower electric oscillations, and with a much less damped wave-train than that employed by the authors. In this case he thought it was possible that the distance between the striæ might give the wave-length of the oscillations.

Dr. RUSSELL remarked that the formation of striations afforded a very convenient means of determining whether a spark was oscillatory or not. The had found the number per cm. along a long tube was nearly constant; in one case it was 22, while with the same spark 30 striations per cm. were obtained on a glass plate.

Dr. MARSH remarked that the distance between the striæ varied with the amplitude even when the frequency was constant. The striæ invervals became slightly smaller along a long tube. Striæ were obtained in progressive wave-trains as well as in stationary waves.

A paper by Prof E. WILSON and Mr. L. C. BUDD on "*Previous Magnetic History as Affected by Temperature*" was taken as read.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting. May 1st, 1911.

Mr. E. Grant Hooper in the Chair.

The following papers were read and discussed:—

"*A Modification of Raschig's Theory of the Lead Chamber Process.*" By Dr. E. Divers.

(This paper was inserted in last week's Chemical News, but inadvertently it was not stated that the paper was read before the London Section of the Society of Chemical Industry, May 1).

"*Testing of Creosote.*" By C. Edward Sage.

The author makes suggestions for a uniform method of testing, and considers that the following are the most important items which should receive attention in any standard specification.

Origin.—The creosote must be the product of the destructive distillation of bituminous coal, and be free from admixture with other oils.

Sampling.—The samples for testing must be obtained from the bulk, below the surface of any floating water; six half-gallon portions to be drawn from different parts of the tank, and mixed. At least three half-gallon samples to be sealed up for analysis or reference.

Specific Gravity.— D $\frac{60^\circ}{60^\circ}$ F.

Expansion Coefficient.—100 cc. to be measured at 40° C., and warmed to 80° C. in a flask graduated on the neck. The increase in volume for this range to be recorded. The average figure found by the author was 1 per cent for each 13·3° C.

Flash-point.—To be taken by means of a Pensky-Marten apparatus.

Fluidity or Condition.—The oil must remain fluid for six hours at a temperature, say, 38° C.

Solubility in Benzol.—Not more than 0·25 per cent to remain insoluble in benzol.

Distillation.—To be made in an 8 oz. retort of the shape and size specified by the author. The retort to be covered with asbestos during the whole distillation. The thermometer employed to be a standardised one with a range of 170—360° C., and the bulb to be placed in the distilling liquid about half an inch from the bottom of the retort. Fractions to be collected:—Under 210° C.; from 210—235°, 235—270°, 270—315°; undistilled at 315° C. The portion distilled to remain fluid or soft on cooling. The collected fractions to be measured at 60° C.

Water.—Some limit should be set as to the amount allowable.

Naphthalene.—To be filtered from the fractions boiling below 270° C. after cooling, pressed between filter-papers, and weighed.

Tar Acids.—To be determined in the portion distilling below 315° C. and the results stated as such.

Pyridine Bases.—To be determined in the portion distilling below 315° C.

Sulphonation.—The fractions distilling between 300° and 315° to be sulphonated, and the residual paraffins measured. The maximum amount to be limited to 0·5 per cent.

Refractive Index.—The fractions distilling above 300° to have a refraction exceeding 1·60 at 60° C.

Curves for the index of refraction of the various distillates of coal-tar creosote and blast-furnace creosote show how the two products differ in this respect.

Biological tests made in the author's laboratory indicated the importance of testing the germicidal value of creosote intended for use in the manufacture of disinfectants and sheep dips. It is suggested that this item should be included in the tests of creosote.

NOTICES OF BOOKS.

Micro-organisms and Fermentation. By Alfred Jörgensen. Translated by S. H. Davies, M.Sc. Fourth Edition. London: Charles Griffin and Co., Ltd. 1911. (15s. net).

Very little has been published in English on the technical applications of microbiology, and this book, which deals with the industrial use of different types of yeast, may be said practically to cover fresh ground. The fourth edition is based upon the fifth German edition, and in it many fundamental alterations have been made. These include the full treatment of the fermentation of milk and other dairy products, and lengthy discussions of the nature and action of the enzymes and of the conditions of yeast nutriment. New methods of cleansing and disinfecting in the fermentation industry are also described, and the practical applications of the research work which has been done on the yeasts are fully noted. English microbiologists will heartily welcome this new edition, and technologists interested in the brewing and other industries will find the work a valuable and comprehensive guide to the most recent developments of the subject.

A Text-book of Organic Chemistry. By A. F. Holleman, Ph.D., F.R.A.Amst. Edited by A. Jamieson Walker, Ph.D. (Heidelberg), B.A., assisted by Owen E. Mott, Ph.D. (Heidelberg). Third English Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1910. (2.50 dols.)

Perhaps no other single work on organic chemistry has been so widely used as this, which is well known in Holland, England, Germany, Italy, and Russia, and thoroughly deserves its popularity. Of the third edition French and Japanese translations are being prepared, so that it may be assumed that the coming generation of chemists of all nationalities will be perfectly familiar with their "Holleman," and from it will have obtained a thorough grounding in the principles of organic chemistry. The chief changes in the third edition, which has followed very closely on the heels of the second, is the re-writing of the pages on the proteins. The classification adopted by the Chemical Society of London and other Chemical and Biochemical Societies is introduced, and these few pages give an excellent short account of the present state of our knowledge of the proteins, including brief allusions to Fischer's method of synthesising polypeptides. Some other small alterations and additions have also been made, and the translator has subjected the whole text to a very careful revision.

University College of North Wales Calendar. Manchester: J. E. Cornish, Ltd. 1910.

We have recently received the Calendar of the University College of North Wales, which besides containing the syllabuses of the different courses for the sessions 1910 1911 gives many further details of the work and regulations of the College, and a short account of its history, with lists of scholarships and awards. Students who have the intention of taking a degree course of the University of North Wales cannot do better than get a copy of this Calendar.

Merck's Index. Third Edition. Darmstadt: E. Merck. (6s. 6d.).

The third edition of this useful catalogue of reagents, drugs, preparations, and minerals has been brought thoroughly up to date, and a good many important additions have been made to it. The scope, however, remains the same, and the list is sufficiently well known to chemists and druggists to need no recommendation as a valuable compilation in which are tabulated the properties of all reagents and preparations for analytical and microscopic work, as well as of drugs and medicines.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 10, March 6, 1911.

Action of Chlorocarbonic Ether on Sodium Ketones.—A. Haller and Edouard Bauer.—When aliphatic ketones of formula $R_3.C.CO—CH<^{R_1}_{R_2}$, or mixed ketones $C_6H_5.CO.CH<^{R}_{R_1}$, are treated with sodamide and chlorocarbonic ether, the following carbethoxylic ethers are obtained:—

$$R_3.C(OCO_2C_2H_5)=C<^{R_1}_{R_2}, \qquad C_6H_5—C(OCO_2C_2H_5)=C<^{R_1}_{R_2}.$$

With the ketones, $C_6H_5.CO.CH_2.R$, the mixed compounds

$$C_6H_5—C(OCO_2C_2H_5)=C(R)—CO_2C_2H_5$$

are formed, and are then split up by the alcoholic soda into sodium carbovinate and monalkylbenzoylacetic ethers. By the same processes acetophenone yields β-carbethoxycinnamic ether, from which benzoyl acetic ether and sodium carbovinate are obtained. Cyclohexanone yields carbethoxycyclohexene.

Radio-active Minerals of Madagascar.—A. Lacroix.—Radio-active minerals are found chiefly in the south and west of Madagascar. They are niobates, niobotantalates, or niobotitanates, and may be divided into two groups; the first includes hatchettolite and microlite, while the second group comprises fergusonite, samarskite, euxenite, and blomstrandite.

Silicon Chlorobromides and Chloroidides.—A. Besson and L. Fournier.—Under the action of the silent discharge, hydrogen and silicon tetrachloride yield chlorides of the general formula Si_nCl_{2n+2}, while in the same circumstances $SiBr_4$ undergoes no reaction. If, however, hydrogen and bromine are allowed to act simultaneously on the tetrachloride, the chlorobromides, $SiCl_3Br$, $SiCl_2Br_2$, $SiClBr_3$, are formed. Mixtures of hydrogen and iodine behave similarly, but the authors have not yet thoroughly investigated the formation of chloroiodides.

Action of Potassium Carbonate on Magnesium Chloride and on Solutions of Magnesium Salts in General. M. Nanty.—The author gives a graphic representation of the results obtained when aqueous solutions of potassium bicarbonate and magnesium chloride are mixed. The first precipitate formed is $MgCO_3.KHCO_3.4H_2O$, and then $MgCO_3.3H_2O$ results.

Butyl Cyclohexane Derivatives.—G. Darzens and H. Rost.—By hydrogenating butyl phenol and its homologues hexahydrophenols are obtained, and may be oxidised to form the corresponding cyclohexanones which are ketones capable of undergoing many transformations. The authors have thus prepared parabutylcyclohexanone, methyl and dimethyl butylcyclohexanone.

Azoderivatives of Phenylisoxazolone.—André Meyer.—By dissolving phenylisoxazolone in a sufficient excess of alkaline liquid and adding sodium acetate, crystalline compounds, insoluble in water, are obtained. They may be regarded as oxyazo derivatives of phenyl-oxy-isox-azol. The author describes the properties of many such compounds, *e.g.*, metanitrobenzene—azophenylisoxazolone, $C_{15}H_{10}O_4N_4$.

MISCELLANEOUS.

Professor H. E. Armstrong, F.R.S.—A banquet in honour of Prof. Henry E. Armstrong is to be held in the Victoria Hall, Hotel Cecil, on May 13, and among those who have notified their intention of being present are Sir Owen Roberts, Sir James Dewar, Sir William Crookes, Sir William H. White, Mr. Charles Lavers-Smith, Prof. W. E. Dalby, Dr. Rudolph Messel, and Mr. Phipson Beale, K.C., M.P.

Royal Institution.—On Tuesday next, May 16, at 3 o'clock, Prof. F. W. Mott begins a course of two lectures at the Royal Institution on "The Brain and the Hand"; on May 18 Dr. W. N. Shaw, Director of the Meteorological Office, delivers the first of two lectures on "Air and the Flying Machine—(1) The Structure of the Atmosphere and the Texture of Air Currents, (2) Conditions of Safety for Floaters and Fliers"; and on Saturday, May 20, Mr. W. P. Pycraft commences a course of two lectures on "Phases of Bird Life—(1) Flight, (2) Migration." The Friday Evening Discourse on May 19 will be delivered by Prof. R. W. Wood on "Recent Experiments with Invisible Light," and on May 26 by Prof. Gilbert Murray on "The Greek Chorus as an Art Form."

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 8th instant; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. C. W. Andsell, Lady Bell, Mr. S. Z. de Ferranti, Mr. H. Kahn, Mr. G. Manuel, Mr. C. E. Moulton, and Mr. A. Perks were elected Members. It was announced from the Chair that the following gentlemen had been nominated as Vice-Presidents for the ensuing year:—The Right Hon. Sir Henry Burton Buckley, P.C.; Right Hon. Earl Cathcart; Dr. Donald W. C. Hood; Mr. H. F. Makins; Sir Francis Laking, Bart.; Mr. Alexander Siemens; Sir James Crichton-Browne (Treasurer); and Sir William Crookes (Honorary Secretary).

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Royal Society of Arts, 8. (Cantor Lecture). "Rock Crystal, its Structure and Uses," by Dr. A. E. H. Tutton.

TUESDAY 16th.—Royal Institution, 3. "The Brain and the Hand," by Prof. F. W. Mott, M.D., &c.

WEDNESDAY, 17th.—Royal Society of Arts, 8. "Les Basses Températures," by Prof. Raoul Pictet.

—— Microscopical, 8. "Method of Disintegrating Bacteria and other Organic Cells," by J. E. Barnard. "Structural Details of *Coscinodiscus asteromphalus*," by J. W. Butcher. Exhibition of Pond Life.

THURSDAY, 18th.—Royal Institution, 3. "Air and the Flying Machine—The Structure of the Atmosphere and the Texture of Air Currents," by Dr. W. N. Shaw, F.R.S., &c.

—— Royal Society. Inbreeding in a Simple Mendelian Stable Population with Special Reference to Cousin Marriage," by S. M. Jacob. "Properties of Colloidal Systems—II., On Adsorption as Preliminary to Chemical Reaction," by W. M. Bayliss. "Distribution and Action of Soluble Substances in Frogs deprived of their Circulatory Apparatus," by S. J. Meltzer. "Transmission of Amakebe by means of *Rhipicephalus appendiculatus*, the Brown Tick," by A. Theiler. "Discrimination of Colour," by F. W. Edridge-Green. "Direct Guaiacum Reaction given by Plant Extracts," by Miss M. Wheldale.

—— Chemical, 8.30. "Some Reactions of ω-Brommethyl-furfuraldehyde," by W. F. Cooper and W. H. Nuttall. "The Course of Chemical Change in Quinol under the Action of Radiant Energy," by W. N. Hartley and O. H. Little. "Method for the Accurate Volumetric Determination of the Oxygen in the Air," by H. E. Watson. "Electrolytic Reduction—IV., Aromatic Aldehydes," by H. D. Law.

FRIDAY 19th.—Royal Institution, 9. "Recent Experiments with Invisible Light," by Prof. R. W. Wood.

SATURDAY, 20th.—Royal Institution, 3. "Phases of Bird Life—Flight," by W. P. Pycraft, F.Z.S.

THE CHEMICAL NEWS.

Vol. CIII., No. 2686.

NEW ORGANIC COMPOUNDS OF NITROGEN.*

By MARTIN O. FORSTER, D.Sc., Ph.D., F.R.S

In the diversity of behaviour exhibited by its derivatives, nitrogen is unrivalled by any other element. This is illustrated not only by the contrasting properties of ammonia, hydrazine, and azoimide, substances composed solely of nitrogen and hydrogen in different proportions, but also by the chemical, physiological, and æsthetic variations displayed by organic compounds of nitrogen, such as nitrocellulose, indigo, azo-dyes, alkaloids, enzymes, and proteins.

Azoimide or hydrazoic acid, HN_3, discovered by Curtius in 1890, is the parent of a series comprising numerous highly reactive organic compounds, the first of which—phenylazoimide—was brought to light by Peter Griess in 1866, after which date the subject lay dormant for more than twenty years. Two methods are applied commercially to the production of sodium azide; the first, described by W. Wislicenus (1892) consisted in passing nitrous oxide over heated sodamide; the second, due to Stollé and Thiele working independently (1908), depending on the interaction of hydrazine, sodium ethoxide, and an ethereal nitrite. In consequence of these, the salt, originally a chemical curiosity, may now be purchased at 40s. per pound, largely owing to the simple and inexpensive preparation of hydrazine devised by Raschig (1908). The principal methods by which organic derivatives of azoimide may be obtained are:—

1. Action of nitrous acid on a substituted hydrazine, applied by Curtius to the production of numerous acyl azoimides.

2. Addition of hydrazoic acid to a diazonium sulphate, found by Noelting to yield aromatic azoimides quantitatively.

3. Interaction of organic halides and sodium azide, as practised at the Royal College of Science in preparing aliphatic azoimides.

It commonly happens that the materials thus obtained are, like the parent compound, explosive; and they are, moreover, very sensitive to light. From a study of their refractive power, it appears that in the aliphatic series the increment of refraction for the triazo-group is 8·91 as compared with 8·93 for bromine; and whilst the atomic dispersion of this halogen is 0·35, that attributable to the triazo-group is 0·36. Moreover, the elevation of boiling-point produced by this complex lies between those due to bromine and iodine, whilst the effect on the dissociation constant of an aliphatic acid exceeds that of iodine, but is less than that of bromine. Thus the physical evidence supports those chemical characteristics which classify the triazo-group as a complex radicle having a strong family resemblance to the halogens.

The changes undergone by triazo-compounds may be referred to one of three main types:—

1. Liberation of two nitrogen atoms in elemental form, leaving the third attached to the carbon which originally carried all three. This is exemplified by triazo-antipyrine, which passes spontaneously into a red azo-compound; whilst in triazoacetone, triazocamphor, and triazoacetic acid the change is accelerated by alkali. Sometimes this type of alteration is violently explosive, as in the case of triazoacetic azide.

2. Unfolding of the three-atom nitrogen ring into a straight chain such as occurs in diazoaminobenzene or in the cycloid tetrazole. Allylazoimide, for instance, a colourless liquid, changes spontaneously into an isomeric solid which no longer contains the triazo-group, whilst hydrazoic acid converts prussic and fulminic acids into tetrazole and hydroxytetrazole respectively.

3. Complete removal of the triazo-group in the form of hydrazoic acid. The simplest example of this change is found in the behaviour of triazomethylamine derivatives, which liberate hydrazoic acid when treated with cold water; this happens also when triazotised carbon is associated with a halogen, as in the case of triazoethylene dibromide, but more generally this type of decomposition requires the action of alkali.

Although the preparation of chloroazoimide by Raschig (1908) indicates the possibility of producing hexatomic nitrogen by the union of two triazo-groups, this new form of the element has not yet been realised.

* Abstract of a Discourse delivered before the Royal Institution, May 5, 1911.

A REVISION OF THE ATOMIC WEIGHT OF NEODYMIUM.*

First Paper.—The Analysis of Neodymium Chloride.

By GREGORY PAUL BAXTER and HAROLD C. CHAPIN

(Concluded from p. 219).

Results and Discussion.

In order to show that no appreciable error occurred owing either to occlusion by silver chloride or from loss of silver chloride in solution, the ratio between the silver used and the silver chloride obtained has been calculated in the five pairs of analyses for which the data are available.

Analyses.	Ag : AgCl.
8 and 16..	0·752663
10 and 17..	0·752726
12 and 19..	0·752626
13 and 20..	0·752686
14 and 21..	0·752621
Average	0·752664

The average ratio of silver to silver chloride is within four thousandths of a per cent of that obtained by Richards and Wells, 0·752634 : 1·000000 (*Pub. Carnegie Inst.*, 1905, No. 28; *Journ. Am. Chem. Soc.*, xxviii., 456).

The results in the preceding tables add further evidence to that already obtained by the spectroscope, that all the samples analysed were of a high degree of purity. Fraction 2923-4 contained all the rare-earth impurities of higher atomic weight than neodymium which accumulated in sixty-seven series of crystallisations, and actually was found to contain a trace of samarium, while fraction 2936-7 contained more praseodymium, probably not more than 0·1 per cent, than any other fraction of the last series which was analysed. The first impurity raises the atomic weight and the second lowers it; yet the difference in the average results of these two extreme fractions is only 0·024. The fractions 1302 and 1614 gave results differing from those of fractions known to be slightly purer by amounts no larger than the experimental error. When corrected for the proportion of the chief impurity, praseodymium, the results agree satisfactorily for all the samples except fraction 2923-4, which certainly contained an unestimated proportion of samarium.

The results obtained from fractions 1302, 1614, and 2923-4 naturally are less reliable than those obtained from the other three fractions. The corrected average for fractions 2926-7-8, 2932-3, 2936-7, is, however, 144·268, which differs from the corrected average for all six fractions, 144·275, by less than 0·01. It is evident that the value 144·27 can safely be taken to represent with accuracy the atomic weight of the purest material which we have

* *Journal of the American Chemical Society*, xxxiii., No. 1.

Atomic Weight of Neodymium.

Series I.—$NdCl_3 : 3AgCl$. (Ag = 107·880, Cl = 35·457).

No. of analysis.	Fraction.	Corrected weight of $NdCl_3$ in vacuum.	Weight of AgCl in vacuum.	Loss on fusion	AgCl dissolved in wash water.	AgCl added in titration.	Corrected weight of AgCl in vacuum.	Ratio—$NdCl_3$:3AgCl.	Atomic weight of neodymium.
		Grms.	Grms.	Grm.	Grm.	Grm.	Grms.		
1.	1302	3·16218	5·42334	0·00030	0·00242		5·42546	0·582841	144·257
2.	1302	2·93305	5·02969	0·00047	0·00304		5·03226	0·582850	144·262
3.	1302	2·99149	5·12978	0·00019	0·00236		5·13195	0·582915	144·289
4.	1302	2·62468	4·50114	0·00030	0·00254		4·50338	0·582825	144·250
						Average		0·582858	144·265
5.	1614	2·38439	4·08848	0·00025	0·00241		4·09064	0·582889	144·278
6.	1614	2·55827	4·38789	0·00029	0·00131		4·38891	0·582894	144·280
7.	1614	3·59114	6·15981	0·00026	0·00140		6·16095	0·582887	144·277
						Average		0·582890	144·278
8.	2923·4	4·27402	7·33208	0·00023	0·00218	0·00200	7·33203	0·582925	144·293
9.	2026 7 8	4·69459	8·06313	0·00029	0·00160	0·01000	8·05444	0·582857	144·264
10.	2926·7·8	2·79574	4·80313	0·00025	0·00142	0·00800	4·79630	0·582895	144·280
						Average		0·582876	144·272
11.	2932·3	2·59810	4·45553	0·00039	0·00227		4·45741	0·582872	144·270
12.	2932·3	3·42064	5 87107	0·00021	0·00196	0·00410	5·86872	0·582860	144·265
13.	2932·3	4·11855	7·06994	0·00018	0·00172	0·00630	7·06518	0·582936	144·298
						Average		0·582889	144·278
14.	2936 7	3·95958	6·79583	0·00017	0·00179	0·00400	6·79345	0·582853	144·262
15.	2936·7	2·71834	4·66295	0·00011	0·00111		4 66395	0·582841	144·257
						Average		0·582847	144·260
						General average ..		0·582876	144·272

Series II.—$NdCl_3 : 3Ag$. (Ag = 107·880, Cl = 35·457).

No. of nalysis.	Fraction.	Corrected weight of $NdCl_3$ in vacuum.	Weight of Ag in vacuum.	Weight of Ag added.	Corrected weight of Ag in vacuum.	Ratio—$NdCl_3$: 3Ag.	Atomic weight of neodymium.
		Grms.	Grms.	Grm.	Grm.		
16.	2923·4	4·27402	5·51825	0·00030	5·51855	0·774482	144·283
17.	2926·7·8	2·79574	3·60989	0·00041	3·61030	0·774379	144·249
18.	2932·3	2·77391	3·58159	0·00037	3·58196	0·774411	144·259
19.	2932·3	3·42064	4·41676	0·00019	4·41695	0·774435	144·267
20.	2932·3	4·11855	5·31786	0·00000	5·31786	0·774475	144·280
		Average				0·774440	144·269
21.	2936·7	3·95958	5·11284	0·00050	5·11289	0·774431	144·266
22.	2936·7	4·64435	5·99649	0·00041	5·99699	0·774447	144·271
		Average				0·774439	144·269
		General average				0·774437	144·268
		Average of all the results in Series I. and II...					144·270

Results Averaged by Fractions.

Fraction . . .	1302	1614	2923-4	2926-7-8	2932-3	2936-7.	Average.
$NdCl_3 : 3AgCl$	144·265	144·278	144·293	144·272	144·278	144·260	144·274
$NdCl_3 : 3Ag$	—	—	144 283	144·249	144·269	144·269	144·268
Average of all individual analyses	144·265	144·278	244·288	144·264	144·273	144·264	144·272
Corrected for praseodymium	144·273	144·284	144·288	144·264	144·273	144·268	144·275

succeeded in preparing. This value is essentially identical with the one chosen by the International Committee upon Atomic Weights, 144·3, and lies midway between the results of Auer von Welsbach and Feit Przibylla on the one hand and that of Holmberg on the other.

We are indebted particularly to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels as well as to the Welsbach Light Company for the neodymium material.

Summary.

1. It is emphasised that crystallisation in more than one form is advisable for the preparation in a pure state of salts of rare earths.

2. The preparation of a very pure neodymium salt is described.

3. The absorption spectrum of neodymium is described

4. A method of obtaining anhydrous neodymium chloride is given.

5. The specific gravity of anhydrous neodymium chloride is found to be 4·134 at 25°/4°.

6. The most probable value of the atomic weight of neodymium is found to be 144·27, if silver is taken at 107·88; with silver at 107·87 neodymium becomes 144·26.

ORGANIC AMALGAMS: SUBSTANCES WITH METALLIC PROPERTIES COMPOSED IN PART OF NON-METALLIC ELEMENTS.*

By HERBERT N. McCOY and WILLIAM C. MOORE.†

A. *Introduction.*

During the last two decades a vast amount of experimental evidence has been accumulating that electricity is granular in structure, though such a conclusion was strongly indicated three-quarters of a century ago by Faraday's discovery of the facts epitomised in the law of electrochemical equivalents, as first pointed out by Helmholtz in 1881. The ultimate granules of electricity are the electrons. The charge of the electron is negative in sign. In fact we have decisive experimental evidence of only this one kind of free electricity, positive electrification of a body being from this standpoint merely a deficiency of electrons.

J. J. Thomson (*Phil. Mag.*, 1904, i., 237) has shown how, from the conception of an atom made up of electrons rotating in a sphere of positive electrification, there follows a simple explanation of many of the properties of an atom, including valence: a univalent atom, if negative, being one that can gain an electron; if positive, one that can lose an electron. A bivalent atom can gain or lose two electrons, a trivalent atom three, &c. According to this hypothesis, the most fundamental property of an atom is this tendency to gain or lose one or more electrons. The tendency to lose electrons is greatest for the alkali metals and least for the noble metals. The tendency to gain electrons is small for sulphur and great for the halogens, the maximum being reached in fluorine. According to this view, for example, sodium and chlorine react with great energy because of the great tendency for each atom of free sodium to lose an electron, on the one hand, and each atom of free chlorine to take up an electron, on the other. The action consists, therefore, in the transfer of an electron from an atom of sodium to an atom of chlorine (Thomson, "The Corpuscular Theory of Matter," p. 120, New York, 1907). The components of the molecules of solid salt are therefore not an *atom* each of sodium and chlorine, but an *ion* of sodium combined with an *ion* of chlorine, if by the term *ion* we now mean an atom ± an electron. The more or less complete "electrolytic dissociation" or "ionisation" which occurs upon dissolving a salt in water is then due to the marked lessening of the electric force which holds together the ions of the solid salt by reason of the very great dielectric constant of water (Thomson, *Phil. Mag.*, 1893, xxxvi., 320; Nernst, *Z. Physik. Chem.*, 1894, iii., 531).

The application of the electron theory to the metallic state by Riecke, Drude, Lorentz, Thomson, and others had led to results of the highest significance. Though the details of the relations of the electrons to the atoms are viewed somewhat differently by various physicists, it is however agreed by those who are working in this field that metals owe their most characteristic metallic properties of a *physical* nature to the *mobile* or free electrons which they contain. The absence of metallic properties in the solid non-metallic elements is, by this hypothesis, due to the supposed tendency of the atoms of such elements to *gain*, not lose, electrons, for which reason such a non-metallic solid will contain very few free or mobile electrons.

Thus, according to one view, the electrons, which are perhaps as numerous as the atoms of the metal, move about freely among the atoms, with which they are considered to be in kinetic equilibrium. Electric conductivity is then due to the drift of these electrons under the influence of the potential in the wire. Thermal conductivity of metals is explained equally satisfactorily by the electron hypothesis. The calculated ratio of thermal to electrical conductivity and also the temperature coefficient of the ratio are in good agreement with the facts. Other metallic properties, including opacity to light, reflecting and radiating power, the Hall effect, the Thomson effect, the Peltier effect, &c., are equally well accounted for.

The most characteristic *chemical* property of a metal is its ability to form the positive ions of salts. Every true metal has this property well developed. If we electrolyse a solution of a salt, say silver nitrate, the free positive ions of silver are attracted and move toward the negative electrode, on coming in contact with which the ion has forced into it an electron, which converts it into an atom of silver. The aggregation of such atoms has metallic properties owing to the great tendency of each atom to give up an electron.

While the atom of any true metal can by loss of one or more electrons form the + ion of a salt, there are of course large numbers of salts, mostly organic, whose + ions are not the residues of metallic atoms. These salts have most of the properties characteristic of salts derived from true metals, but are distinguished from the latter by the fact that they are the derivatives of the "compound radicals." When we consider, theoretically, the behaviour upon electrolysis of a salt of a base-forming compound radical it is difficult to see wherein the result should differ from that obtained with a salt of a metallic element. In this case, as in the other, positive ions are attracted to the cathode and upon striking it can gain electrons. If the electron theory of the metallic state is as fundamental as it seems to be, there would be little reason to doubt that the aggregate of such free radicals would be a body having metallic properties; for such a hypothetical body would be made up of radicals which, analogous to metallic atoms, could easily lose electrons. The mass would then contain an abundance of mobile or free electrons, and in such case would possess high electrical and thermal conductivity, metallic lustre, &c. Practically, however, several causes may prevent the isolation of such metallic substances. We know that it is not possible to separate by electrolysis many metals from aqueous solutions of their salts. This is the case with sodium, whose electric solution tension exceeds that of hydrogen by so much that the latter element is liberated from the water by the current and no sodium is obtained on the electrode. Similar relations may obtain in the electrolysis of an organic salt, as is shown in the experimental part. On the other hand, it is theoretically possible that such a compound metal may be so unstable in the free state that it suffers spontaneous decomposition at the moment of its formation from its ions. A third possibility is exemplified by the case of hydrogen. For a long time it was thought by some chemists that hydrogen in the solid form would have metallic properties, since acids may be considered "hydrogen salts." The fact that solid hydrogen is now known to have no metallic properties proves clearly the fallacy of the old idea and seems also to be a flat contradiction of our hypothesis. (In some cases, however, hydrogen seems to have some properties of a metallic character: it dissolves readily in palladium, and, when nascent, diffuses easily through iron—Bellati and Lussana, *Z. Physik. Chem.*, 1891, vii., 229). Now hydrogen differs from the metals in one other important respect: while the molecules of metallic vapours are always monatomic those

* Preliminary report read at the Detroit Meeting of the American Chemical Society, June, 1909 (*Science*, 1909, xxx., 315). From the *Journal of the American Chemical Society*, xxxiii., No. 3.

† The final part of the experimental work of this investigation was carried out at the Columbia University after my removal from Chicago to Columbia. I wish here to make acknowledgment of the many courtesies shown me by several of my colleagues in the Havemeyer Laboratories.—William C. Moore.

of hydrogen are diatomic. Thomson has considered the question of the theory of the union of two like atoms to form a molecule of an elementary gas, and has shown very convincingly that it is reasonable to conclude that one atom sends its valence electron into the other, and that the combination is entirely analogous to that when two unlike atoms combine. If this is the case it is possible to understand why solid hydrogen has no metallic properties; its valence electrons are bound and not *free* or *mobile*. It is possible that some positive organic ions will behave like hydrogen when set free and unite in pairs to form double radicals. These would not be expected to have metallic properties, the valence electrons being bound. Turning now from theory to facts, we find that there is already considerable evidence that free electropositive radicals have metallic properties. The case of ammonium amalgam is familiar to every chemist. This remarkable substance was discovered by Seebeck (*Ann. Chem.*, 1808, xvi., 191) and practically simultaneously by Berzelius and Pontin. Davy (*Phil. Trans.*, 1810, 37) compared ammonium amalgam with the amalgams of sodium and potassium, and was led to announce his famous ammonium hypothesis: the radical ammonium was analogous to the alkali metals and was said to exist in metallic form, united with mercury, in the amalgam. Berzelius and Ampere also supported this view. On the other hand Gay-Lussac and Thenard (see Routledge, Chem. News, 1872, xxvi., 210) concluded that the so-called amalgam is only a mixture of ammonia, hydrogen, and mercury, a view shared by many others, among them Seeley (Chem. News, xxi., 265), who found the volume of the inflated mass to be inversely proportional to the pressure upon it. The case against the metallic ammonium hypothesis was made still stronger by the evidence furnished by Landolt (*Ann. Chem.*, 1868, vi., 346), who was unable to precipitate from solutions of their salts either copper or silver by means of ammonium amalgam.

The first really convincing evidence in favour of the ammonium hypothesis was furnished by Le Blanc (*Z. Physik. Chem.*, 1890, v., 467), who electrolysed a solution of an ammonium salt with a mercury cathode. The apparatus was so arranged that simultaneous measurements of the polarisation potential could also be made. This potential rose in a few minutes to a maximum which was nearly as great as that given by sodium salt. The really important result, however, was observed after the polarising current was cut off. The mercury cathode, which showed the inflation characteristic of ammonium amalgam, was still strongly electronegative toward the solution and remained so for ten to twenty minutes. This effect was not due to hydrogen, it having been shown that the hydrogen polarisation potential was considerably smaller and that it fell off almost as soon as the current was interrupted. Coehn (*Z. Anorg. Chem.*, 1900, xxv., 430) next showed that the failure of Landolt's experiment was due to too high a temperature. Ammonium amalgam prepared at 0° would precipitate copper from the sulphate without difficulty. This result was of itself insufficient to prove the metallic nature of ammonium, since free hydrogen was always present in the amalgam and may have been the active substance in the reaction. To remove any doubt Coehn then showed that not only are cadmium and zinc precipitated by the cold amalgam but that barium amalgam results from the action, at zero, of ammonium amalgam on a solution of barium chloride. This fact was independently discovered later by G. M. Smith (*Journ. Am. Chem. Soc.*, 1907, xxix., 844), who also obtained sodium and potassium amalgam in a similar manner. Thus the experiments of Le Blanc, Coehn, and G. M. Smith furnish indisputable evidence of the metallic nature of ammonium in ammonium amalgam. Le Blanc's polarisation experiments also included the study of the salts of a number of substituted ammonias. Mono-, di-, and tetramethyl and monoethyl ammonium ions gave results more or less like those shown by ammonium, from which facts Le Blanc concluded that in these cases also amalgams were formed, although none of the supposed amalgams were isolated.

In the present investigation we have isolated two of these organic amalgams and have demonstrated beyond question their metallic nature, and have thereby furnished additional evidence of the possibility of the preparation of substances with metallic properties composed in part of non-metallic elements.

B. *Preparation of Tetramethyl Ammonium Amalgam.*

The first attempts at the preparation of tetramethyl ammonium amalgam were made by the action at 0° of 8 per cent sodium amalgam on a 25 per cent aqueous solution of tetramethyl ammonium chloride. Hydrogen was given off, but no new product resulted. The electrolysis of aqueous solutions of the chloride under various conditions of temperature and concentration gave always colloidal mercury at the mercury cathode, but no amalgam could be isolated. It was thought that an amalgam might be formed by the action of the current and be rapidly decomposed by the water. Accordingly, absolute alcohol was substituted for water as solvent and proved wholly satisfactory.

The first successful preparation of tetramethyl ammonium amalgam was accomplished by the electrolysis of a saturated solution of tetramethyl ammonium chloride in absolute alcohol, using a platinum anode and a mercury cathode. The temperature was $-10°$. By means of a potential-reducing device, the direct current of the lighting circuit (110 volts) was cut down to 18 volts, and the current was allowed to run at this pressure for thirty minutes. As prepared in this way, the amalgam is a stiff mixture of shining crystals of the amalgam and the excess of mercury; it is but very slightly inflated, silvery white in colour, and decidedly metallic in appearance. (When properly prepared, it shows at temperatures below $+10°$ absolutely no tendency to become inflated, in which respect it differs markedly from ammonium amalgam). In contact with alcohol it is moderately stable, but reacts violently with water.

Since this first preparation was made the amalgam has been prepared by this method many times and many of its properties studied. However, since in using a platinum anode chlorine is evolved, the method has been improved by the substitution of an anode of silver-plated platinum gauze.

In the most convenient form of apparatus for the production of the amalgam, a small Gooch funnel is used as the electrolytic chamber. This is supported by passing the stem through a one-hole rubber stopper, closing the tubulure of an inverted four-litre bell-jar, which serves as an ice chamber. The whole apparatus is supported at an appropriate height, by means of a ring and a universal clamp, on an iron stand. A piece of rubber tubing fastened to the stem of the Gooch funnel, and closed by a pinch-cock, affords a convenient outlet for the amalgam after it is formed. The anode consists of a piece of silver-plated platinum gauze rolled into cylindrical form. This gauze is welded to a stout platinum wire which passes between the edge of the funnel and the rubber stopper closing the funnel. The negative wire, insulated by a glass capillary tube, enters the funnel through one leg of a T-tube. The upper end of this T-tube, where the wire enters, is closed by means of universal wax or a glass cap and a piece of rubber tubing, while a calcium chloride tube is attached to the other leg of the T to exclude moisture. A thistle-tube, reaching almost to the mercury cathode, is inserted into the second hole in the rubber stopper, and serves for the introduction of mercury or of the electrolyte.

Fitted up in this manner, the procedure for making a "run" with the apparatus is as follows:—The mercury to serve as a cathode is run into the electrolysis chamber through the thistle-tube; the solution of the electrolyte is then introduced, the bell-jar having previously been filled nearly to the top of the Gooch funnel with crushed ice or a freezing mixture. The current is then turned on, the

potential and strength being regulated so that about 0·25 ampère passes through the cell, under ordinary circumstances. After running for ten to fifteen minutes, the current is interrupted; the excess of mercury run off through the delivery-tube at the bottom of the apparatus into a dry dish; the amalgam is then run off into a second dry dish and used as desired, while the excess of mercury is poured, through the thistle-tube, back into the electrolytic cell. In this way a number of successive runs can be made with but little interruption.

To be continued).

ANALYSIS OF CRUDE GLYCERIN.

(Concluded from p. 221).

Acetin Process for Glycerol Determination.

This process is the one agreed upon at a conference of Delegates from the American, British, French, and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on crudes in general, and is the process to be used (if applicable) whenever only one method is employed. On pure glycerins the results are identical with those of the bichromate process. For the application of this process the crude glycerin should not contain over 50 per cent water.

Reagents Required.

A. *Best Acetic Anhydride.*—This should be carefully selected. A good sample must not require more than 0·1 cc. normal NaOH for saponification of the impurities when a blank is run on 7·5 cc. Only a slight colour should develop during digestion of the blank.

B. *Pure Fused Sodium Acetate.*—The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly, and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous.

C. *A Solution of Caustic Soda for Neutralising, of about* N/1 *Strength, Free from Carbonate.*—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide), and allowing to settle until clear, or filtering through an asbestos or filter-paper. The clear solution is diluted with water free from carbon dioxide to the strength required.

D. N/1 *Caustic Soda, Free from Carbonate.*—Prepared as above, and carefully standardised. Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

E. N/1 *Acid.*—Carefully standardised.

F. *Phenolphthalein Solution.*—0·5 per cent phenolphthalein in alcohol, and neutralise.

The Method.

Into a narrow mouthed flask (preferably round bottomed), capacity about 120 cc., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1·25 to 1·5 grms. of the glycerin. Add first about 3 grms. of the anhydrous sodium acetate, then 7·5 cc. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside.

The flask is connected to the condenser by either a ground glass joint (preferably), or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapour.

Heat the contents, and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 cc. of the carbon-dioxide-free distilled water heated to about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding the water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80° C. until the solution is complete except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion, solution is more quickly effected. Cool flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper or ground glass connection into the flask, and filter contents of flask through an acid washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 cc. of phenolphthalein solution (F), then run in a caustic soda solution (C) or (D) until a faint pinkish yellow colour appears throughout the solution. This neutralisation must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 cc. or a calculated excess of N/1 NaOH (D), and note carefully the exact amount. Boil gently for fifteen minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate excess of NaOH with N/1 acid (E until the pinkish yellow or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end-point taken.

From the N/1 NaOH consumed calculate the percentage of glycerol after making the correction for the blank test described below. 1 cc. of N/1 NaOH = 0·03069 grm. o glycerol.

The co-efficient of expansion for normal solutions is approximately 0·00033 per cc. for each degree C. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralising the acetic acid, it is not necessary to add more than 5 cc. of the N/1 alkali (D), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

Determination of the Glycerol Value of the Acetylisable Impurities —The total residue at 160° C. is dissolved in 1 or 2 cc. of water, washed into a clean acetylising flask 120 cc. capacity and the water evaporated. Now add anhydrous sodium acetate and proceed as in the glycerol determination before described. Calculate the result to glycerol.

Analysis of Acetic Anhydride.—Into a weighed stoppered vessel, containing 10 to 20 cc. of water, run about 2 cc. of the anhydride, replace stopper and weigh; allow to stand, with occasional shaking, for several hours, till all anhydride is hydrolysed; then dilute to about 200 cc., add phenolphthalein and titrate with N/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride. Into a stoppered weighing-bottle containing a known weight of recently distilled aniline (from 10 to 20 cc.) measure about 2 cc. of the sample, stopper, mix, allow to cool, and weigh. Wash contents into about 200 cc. cold water, and titrate acidity as before. This yields the acidity due to the original, performed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second

result from the first (both calculated for 100 grms.) and double result, obtaining cc. N/1 NaOH per 100 grm. sample. 1 cc. NaOH equal 0·0510 anhydride.

Bichromate Process for Glycerol Determination.

Reagents Required.

A. *Pure Potassium Bichromate* powdered and dried in air free from dust or organic vapours at 110° to 120° C. This is taken as the standard.

B. *Dilute Bichromate Solution.*—7·4564 grms. of the above bichromate (A) are dissolved in distilled water and the solution made up to 1 litre at 15·5° C.

C. *Ferrous Ammonium Sulphate.*—Dissolve 3·7282 grms. of potassium bichromate (A) in 50 cc. of water. Add 50 cc. of 50 per cent (by volume) sulphuric acid, and to the cold undiluted solution add from a weighing-bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate.

D. *Silver Carbonate.*—This is prepared as required for each test from 140 cc. of 0·5 per cent silver sulphate solution by precipitation with about 4·9 cc. of N/1 sodium carbonate solution (a little less than the calculated quantity of N/1 sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling). Settle, decant, and wash once by decantation.

E. *Subacetate of Lead.*—Boil a pure 10 per cent solution of lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

F. *Potassium Ferricyanide.*—A very dilute solution containing about 0·1 per cent.

The Method.

Weigh 20 grms. of the glycerin, dilute to 250 cc., and take 25 cc. Add the silver carbonate, allow to stand, with occasional agitation, for about ten minutes, and add a slight excess (about 5 cc. in most cases) of the basic lead acetate (E), allow to stand a few minutes, dilute with distilled water to 100 cc., and then add 0·15 cc. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow mouthed vessel rejecting the first 10 cc., and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 cc. is ample). Occasionally a crude will be found requiring more, and in this case another aliquot of 25 cc. of the dilute glycerin should be taken and purified with 6 cc. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 cc. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3·7282 grms. of the powdered potassium bichromate (A). Rinse down the bichromate with 25 cc. of water, and stand with occasional shaking until all the bichromate is dissolved (no reduction will take place).

Now add 50 cc. of 50 per cent sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapours, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 grm. glycerol equals 7·4564 grms. bichromate.
1 grm. bichromate equals 0·13411 grm. glycerol.

Notes.

1. It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

2. Before the bichromate is added to the glycerin solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

3. For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0·5 cc.

4. It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

Instructions for Calculating Actual Glycerol Content.

1. Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities if any be present.

2. Determine the total residue at 160° C.

3. Determine the acetin value of the residue at (2) in terms of glycerol.

4. Deduct the result found at (3) from the percentage obtained at (1), and report this corrected figure as glycerol. If volatile acetylisable impurities are present these are included in this figure.

Notes and Recommendations.

Experience has shown that in crude glycerin of good commercial quality the sum of water, total residue at 160° C., and corrected acetin result comes to within 0·5 of 100. Further, in such crudes the bichromate result agrees with the uncorrected acetin result to within 1 per cent.

In the event of greater differences being found, impurities such as polyglycerols or trimethylene glycol are present. Trimethylene glycol is more volatile than glycerin; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and bichromate results of such distillates. Trimethylene glycol showing by the former method 80·69 per cent and by the latter 138·3 per cent expressed as glycerol.

In valuing crude glycerin for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates. The methods for detecting and determining these impurities have not formed the subject of this investigation.

(Signed) Otto Hehner, Chairman.
John Allan.
James B. McArthur.
W. H. Phillips.
P. Tainsh.
Frank Tate.
J. L. Buchanan, Hon. Secretary.

Recommendations by Executive Committee.

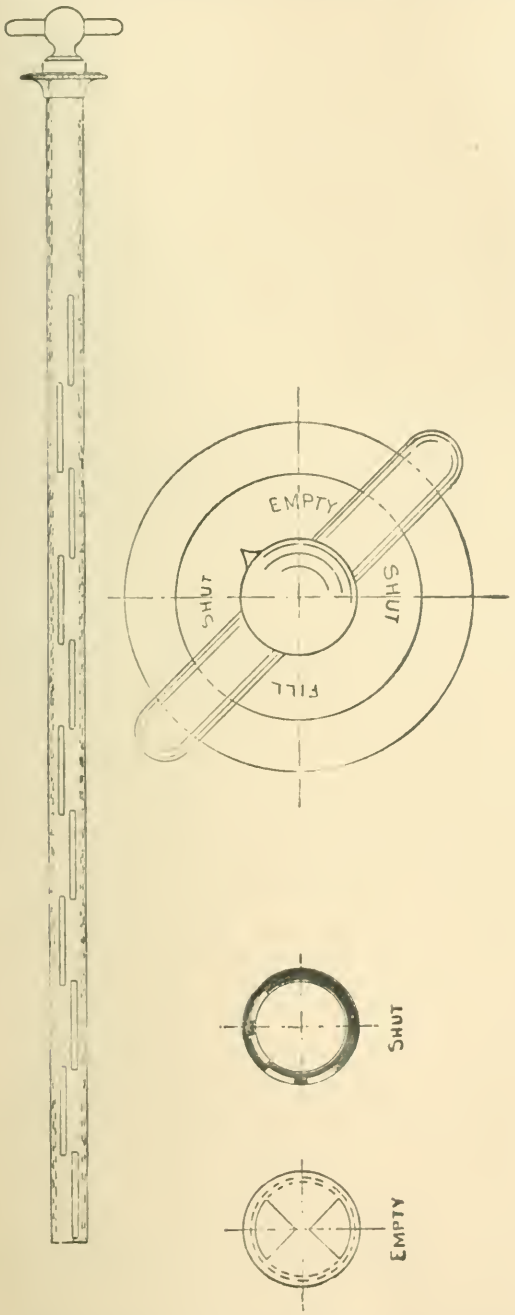
If the non-volatile organic residue at 160° C. in the case of a soap lye crude be over 2·5 per cent, *i.e.*, when not corrected for carbon dioxide in the ash, then the residue shall be examined by the acetin method, and any excess of glycerol found over 0·5 per cent shall be deducted from the acetin figure.

In the case of saponification, distillation, and similar glycerins, the limit of organic residue which should be passed without further examination shall be fixed at 1 per cent. In the event of the sample containing more than 1 per cent, the organic residue must be acetylated, and any glycerol found (after making the deduction of 0·5 per cent) shall be deducted from the percentage of glycerol found by the acetin test.

Appendix I.—*Sampling Crude Glycerin.*

The usual method of sampling crude glycerin hitherto has been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerin contained in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates viscous glycerins run into the tube very slowly, so, owing to the time occupied, it is impossible to take a complete section of the sample. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

The sampler which is illustrated herewith has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the



ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement the glycerin fills into the sampler almost instantaneously. There are also a number of ports cut at the bottom of the sampler which render it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In samplers of larger section (1 in.) it is possible to arrange a third motion whereby the bottom ports only are open for emptying, but in samplers of smaller dimensions (⅝ in.) this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom the ports are opened for a second or two, then closed and withdrawn, and the sample discharged into the receiving vessel by opening the ports. When the drum contains suspended salt the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum, it is therefore recommended that the drum should be sampled before the salt has settled.

A sampler 1 in. dia. withdraws approximately 10 oz. from a 10 cwt. drum.

A sampler ⅝ in. dia. withdraws approximately 5 oz. from a 10 cwt. drum.

(The authorised makers of the apparatus are Messrs. Young and Co., 45-49, Stanley Street, Kinning Park, Glasgow).

FORMAL OPENING OF THE CHEMISTS' BUILDING, NEW YORK CITY.

The Chemists' Building Company, organised to promote the interests of Chemical Science and Industry in America, has erected a ten-story fireproof building, on a lot 56 feet wide and 100 feet deep, at 50-54 East 41st Street, New York City, close to the Grand Central Station and the 42nd Street Express Station of the Subway, as well as to the prospective termini of the "Steinway" and "McAdoo" tunnel systems; a few minutes' walk from the New York Public Library, Engineering Society's Building, and Academy of Medicine.

The lower half of this building is leased to the Chemists' Club, and contains all the appurtenances of a social club, including excellent apartments, together with a large auditorium for scientific meetings and ample space for a complete chemical library and museum.

The five upper stories have been specially constructed for laboratory purposes, and can be rented either as entire floors, or in suitable subdivisions, to analytical, commercial, or research chemists, physicists, bacteriologists, &c., but not as manufacturing laboratories. The Chemists' Club at present has 334 resident, 368 non-resident, 5 honorary, and 4 life members.

The fourth and fifth stories are residential, and provided with rooms for either transient or permanent occupancy. There are two suites, consisting of sitting-room, bedroom, and bath-room, with a private corridor, and eighteen other bedrooms, a number of which are provided with private bath-rooms. Each suite or room is named after a college or university, whose alumni have furnished it, and this serves to accentuate the academic spirit of the Club membership. The institutions thus commemorated are:—Harvard, Yale, Princeton, Columbia, Pennsylvania, New York University, Massachusetts Institute of Technology, British Schools and Universities, Cornell, Johns Hopkins, German Universities, University of Virginia, University of Michigan, College of the City of New York, Imperial University of Japan, Swiss Universities, Chicago Members.

All the floors are connected by telephone with the central switch-board, on the entrance floor, and the same board serves the tenants of the laboratories in the upper stories.

It is also interesting to note that the Club controls three small laboratories, named in memory of Wolcott Gibbs, Robert Bunsen, and August W. Hofmann, which are equipped for the transient use of Club members. Applications for their use must be made at the Club office.

The dedication exercises were held on the afternoon of March 17th, and were followed by three scientific meetings, a banquet, and music circle.

Prof. Morris Loeb, the President of the Chemists' Building Company, on taking the Chair, speaking on behalf of the directors and stockholders, said that the building was the first of its kind and compared favourably with the Hofmann-Haus of Germany and Faraday Laboratories of London, and pointed out the great advantage that the institution would be to the American chemist, who will now have easy access to books and apparatus and facilities for research, as well as all the social advantages of a first-rate club.

Prof. Loeb's address was followed by speeches of a similar character by Prof. E. W. Morley, of West Hartford, Conn.; Prof. Alexander Smith, President of the American Chemical Society; Prof. Ira Remsen, President of Johns Hopkins University; and Prof. Wilder D. Bancroft, of Cornell University.

Dr. F. W. Clarke, Chief Chemist of the United States Geological Survey, in dedicating the auditorium, gave a brief outline of the life of Rumford, from his birth at Woburn, Massachusetts, to his experience as a teacher in Rumford, now Concord, New Hampshire, and his more noteworthy activities in England and Bavaria. His versatility as an inventor, statesman, and scientific thinker was pointed out, and emphasised by certain curious coincidences and contrasts. He, an American, was the principal founder of the Royal Institution in London, while an Englishman established the Smithsonian Institution in Washington. Rumford first proved the equivalency of heat and motion, and so laid the foundation for the modern conception of the conservation of energy; his second wife was the widow of Lavoisier, who demonstrated the conservation of matter. Sir Humphry Davy once said that his principal discovery was Michael Faraday; Rumford, in a certain sense, might have claimed to have discovered Davy, whom he placed in the Royal Institution. Rumford founded the Rumford medals of the Royal Society and the American Academy, the latter organisation being also his creation. He also endowed the Rumford Professorships in Harvard University.

The bronze tablet was then unveiled. The inscription was:—

This Hall is Dedicated
To the Memory of
BENJAMIN THOMPSON,
COUNT RUMFORD,
1753-1814.

A native of Massachusetts and Alumnus of Harvard College. The first great Chemist of American birth. By the discovery of the Transformation of Mechanical Force into Heat he laid the foundation for the Theory of the Conservation of Energy. His studies in the Economy of Fuel Consumption represent the first conscious effort toward the Conservation of Natural Resources. He was a pioneer in Steam Heating and Domestic Sanitation. He was a pathfinder in Constructive Charity. Driven hence, as was Priestley hither, by neighbourly intolerance, he became a dweller in many lands and a Benefactor to each. Bavaria owed him an administration of unprecedented efficiency and a military system based upon the manhood of the private soldier. To England he gave the Royal Institution, the home of Humphry Davy and of Michael Faraday. At Harvard College he founded the Chair made illustrious by Eben Horsford and Wolcott Gibbs. America received at his hands its first endowment for the encouragement of Research in the Exact Sciences.

Dr. Russell W. Moore, President of the Chemists' Club, in taking over the building, said: It is with great pleasure that I accept this key of the Chemists' Club; at the same time wish to express my appreciation of the earnest endeavour and effort that have given us such a magnificent home. There is everything that the chemist needs. We have just listened to representatives of the chemical societies who have explained the necessity for scientific societies and the proper method of educating chemists. All these institutions can be properly regarded as preparatory courses to membership in the Chemists' Club. Some may ask what the chemical societies are for. No one who enters and walks around this building will need to ask what the Chemists' Club is for. If the colleges and societies have not done their work well there is a complete chemical library where defects of education can be repaired, and if beyond repair we can put them in the museum. This key is a great responsibility, and I can see myself waiting in the hall until the last chemist has gone home and then locking up and hanging its half-pound of iron to my watch chain, and going home myself. But I am glad to accept the responsibility. It was many years before I was trusted even with a small door key, and I never expected to live to see the day when one as large as this would be given me. It is with full confidence that the many wishes for the success of the Chemists' Club will be realised that I accept its key.

The meeting closed with a reception in the Club rooms.

In the evening an extraordinary meeting of the New York Section of the American Chemical Society was held in the building, and the following address was given by Prof. Baskerville, of New York:—

"We may gasp a little for breath at this altitude, but I fancy we like the elevation. From this plane we may look far back; and, as was said a hundred years ago, 'the century which has since passed has seen this (our) Science develop and grow, until men have come scarcely to dare put a limit to its possibilities.' If I know my history, as I look back through the last four centuries, I see clearly three other great terraces in the progress of knowledge.

"The first half of the sixteenth century was an epoch which witnessed the differentiation of chemistry from alchemy. The sciences secured a foothold in the Universities of Oxford, Heidelberg, and others in France and Italy, wherein free exchange of thought was favoured. The story of the University is that of the Liberator. Its climaxes are strikingly coincident with eventful occurrences in the history of our Science. The spirit of freedom from the domination of dogma exerted itself in the Iatro-chemical period, and then it was that Wickliffe, John Huss, and Luther spoke in the halls and from the steps of the Continental universities, as did Colet, Erasmus, and Sir John More in England.

"The Iatro-chemists may have looked through a glass darkly, but there was remarkable prescience in these words, 'The operations which go on in the human body are chemical ones, and the state of health depends upon the composition of the organs and juices.' The inductive method brought experimental chemistry into existence, and chemistry young then—even in its infancy—was ensnared within the meshes of medicine. It gave itself to the making of an apothecary's shop out of an herb and root store.

"A century passed before the reactionary movement of a fixed scientific purpose spread itself out upon the second terrace. From the time of Boyle forward, the great aim of chemistry became the discovery of new chemical facts with the object of arriving at the truth alone. Then it was that lectures were given by Thomasius in the vernacular, which previously had been given only in Latin. This was done in 1700 at Halle, which has been called 'the first modern university.' It was there earliest recognised that the university teacher's duty was not to transmit familiar scholastic philosophy, but to develop independent thinking. Research, which later became the characteristic mark o

the university, was inaugurated. In that time, at the commencement of a period of transition, we find Becher and Stahl, who bridged the gap between empirical chemistry and modern chemistry. To be sure they did not collect the materials for the structure—they did not altogether construct it, but they designed it and greatly assisted in the work of building. It was a poor bridge and built upon shifting sands, but it served as a channel of escape from mysticism, and many passed over to take refuge on the other side. Black, Cavendish, Marggraf, Scheele, Bergman—we need not enumerate them all, for, as Coleridge has said, 'A compendium of names is a non conductor, they stop all interest'—they were all phlogistonists in the truest sense, and in their researches methods are encountered which bear the imprint of new departures and a better understanding of the composition of substances. It was the *qualitative* period. Unity of purpose made possible by the organisation of learned societies characterised the time; and Boyle's axiom that 'only what can be demonstrated to be the undecomposable constituents of bodies are to be regarded as elements,' laid out the straight path to the next eminence.

"Then followed a period of infinite unrest. The Protestant dogmatism of the English Universities caused them to be the nursery of Colonial America. Harvard and Yale were founded by protesting Protestants. The dynamics of democracy produced our national autonomy. There were dissensions even within the circles of science. Facts accumulated upon facts, nearly one-half of our present accepted chemical elements were discovered, but pioneers secured only a reluctant hearing, and some none at all in this period, which involved the beginning of the nineteenth century. Franklin's paper on lightning-conductors was laughed at and not published by the Royal Society. Galvani was attacked by his colleagues, designated a know-nothing, and called the frog's dancing master. The fermier-general, Lavoisier, was publicly executed in France, but not until he had sifted and collated the facts handed down by the phlogistonists and decided that the foundation of all theoretical inferences should be laid upon observations made under definite conditions. One of these conditions involved the balance. The direction of chemical thought was changed, and the facts hitherto ascertained appeared in a new light. It was the *quantitative* period.

"A Frenchman has said that the 'way to make an impression upon the world is to plough through humanity like a cannon ball, or to creep through it like a pestilence.' Some here may liken the atomic theory to one, and some to the other, but it will be recognised by all that through the efforts of Proust, Richter, Dalton, Gay-Lussac, and especially Berzelius, a spirit of order spread all around. We acquired a physical conception of a chemical reaction. At first that was limited to inorganic material, but gradually the discoveries of Wöhler, Liebig, and Dumas, the theoretical discussions of Laurent and Gerhardt, and the physical regularities indicated by Kopp, extended these conceptions to the living world. 'There were to be no baseless and delusive dreams for the future, although mistakes might be made in the interpretation of facts.'

"Now we are at our own times. Had one thirty years ago predicted what we actually know uow, he would have been regarded fit for an asylum. He would have been so judged not only by six expert alienists, but by twelve of his peers as well. We have masters in their fields at hand, and they will tell us where we stand. Events pile on events so rapidly that we can scarcely read the journals, much less pay for them. It is therefore to be assumed that all here are more or less familiar with the interrogation marks placed after the elements, the exclamation symbols which follow the interpolation of metabolic processes, and the period of finality that one finds after the energy concept of matter. Perhaps the air is not so thin after all; only the clouds of the physical conceptions of matter are being swept aside by the chemical conceptions of energy—to return again no doubt."

In introducing Prof. Jacques Loeb, Biologist to the Rockefeller Institute for Medical Research, the Chairman said that—"Medicine is now, in fact, entirely dependent upon chemistry. To quote from a recent lecture of C. A. Keane (*Journ. Soc. Chem. Ind.*, xxix., 383): 'The ambition of the iatro-chemists to explain all metabolic and vitalistic phenomena by chemical means led to the fall of the school; chemistry was then far from ripe for such broad generalisations. The experimental data both in chemistry and in medicine that were accumulated during the succeeding two centuries lacked correlation; and although in many instances vitalistic functions stimulated the chemist to scientific investigations, whilst the chemist on his part was able to place many compounds of therapeutic value in the hands of the practitioner, the close association and interdependence of the two sciences aimed at by the iatro-chemists has only become possible by the development of the borderland studies, chemical physiology and pharmacology, in association with modern organic and physical chemistry. This association, which has been effected with conspicuous and increasing success during the past thirty years, marks the new period of Iatro-chemistry."

Prof. Jacques Loeb gave an address on "The Characteristics of Living Matter from the Physico-chemical Point of View." He reviewed briefly his researches upon the artificial fertilisation of the eggs of the sea urchin. He showed the important *rôle* played by chemistry and physics in the fundamental processes of life—growth and reproduction. These processes are, at bottom, oxidations and hydrolyses, and neutral fertilisation is simply a means to accelerate or inhibit the rate of these chemical changes. The development of an artificial fertilisation membrane may be brought about by the use of fatty acids, *e.g.*, butyric acid—because of the solubility of these acids in this membrane—the more readily soluble, the more rapid the action. Similarly, hypertonic solutions may be used to produce the membrane.

Prof. R. B. Moore read a paper on "The Rare Gases of the Atmosphere" (this paper will be reproduced in full in a future issue), and at its conclusion a vote of thanks to the speakers of the evening was proposed by Dr. Leo H. Baekeland, and seconded by Dr. Charles A. Doremus, and the proceedings then terminated.

On Saturday, the 18th, the following papers were read, some of which will be published in subsequent issues:—

"Mental Catalysis, the Influence and Power of Suggestion in Inaugurating and Prosecuting Research," by Prof. W. R. Whitney, Director of the Research Laboratory of the General Electric Company.

"The Chemistry of Phosphorescence," by Prof. W. D. Bancroft.

"Contributions of Chemistry to Sanitation," by Prof. W. P. Mason.

An Address by the Chairman of the American Electrochemical Society, Mr. Elmer A. Sperry, of Brooklyn.

"History of Chemical Industry in New York City," by Dr. Chas. F. Chandler.

The Chairman then said that in inviting the speakers of the evening it was mildly suggested that the addresses and demonstrations be such as one might hear and see in the Royal Institution of London, founded by Rumford, after whom the Assembly room was named. If Count Rumford had been present he would have been pleased.

Dr. Leo H. Baekeland, in proposing a vote of thanks to the speakers, said after the opening address of Prof. Baskerville, after the inspiring lecture of Prof. Jacques Loeb, after the brilliant work of Prof. Moore, that anything he might say would sound like a sizzling firecracker at the end of magnificent fireworks. But permit me to detain you a few moments more to move a vote of thanks to the lecturers who have contributed to-night to make the first meeting of our Section in the new Clubhouse a memorable one, which I hope will become a pace maker and a new high standard for our future sessions.

Dr. Charles A. Doremus, in seconding the vote of thanks, said:—To me the study of the chemistry of living matter has always been entrancing. Those of us who are citizens of this great City should be proud of the fact that the New York Medical College was the first medical school in this country that not only offered laboratory instruction in the department of chemistry, but made laboratory practice obligatory. From this initiative the custom has spread through the land. But it is only within recent years that medical students have been emancipated from the study of elementary chemistry, that service being now performed in the preparatory schools and colleges, and are thus enabled to enter at once in their special course of study of those chapters directly connected with vital phenomena. When the American Chemical Society was organised in 1876 the illustrious Prof. John W. Draper was elected its first President. A couple of sentences from his scholarly Presidential Address appear to me to have peculiar significance this evening:—

"I often look at the bright yellow ray emitted from the chromosphere of the sun, by that unknown element helium, as the astronomers have ventured to call it. It is trembling with excitement to tell its story, and how many unseen companions it has."

Little did he dream that at the dedication of this beautiful building we should be shown by such accurate and convincing experiments that these very elements were in the air about us, and that when he uttered his prophetic words they helped to tremblingly transmit the sound of his voice to the audience before him.

In closing the meeting the Chairman said:—These splendid new quarters—the outcome of American chemical brotherhood—are simply an expression of the trade union principle of self assertion. Public opinion will now recognise our profession with its dignity, and realise that it is intimately associated with the things that make up life.

In the evening a banquet was given, and over 250 guests were present. In the course of the speeches that followed it was announced that the sum of 250,000 dollars asked for by the Building Company had been over subscribed. The celebrations ended on Sunday afternoon by a musical entertainment by the Olive Mead Quartet.

THE INTERNATIONAL CHEMICAL ENGINEERING EXHIBITION,

Royal Agricultural Hall, Islington, N.

Considering the great developments that are in progress in connection with Chemical Engineering, and the immense national importance of the subject, it is but fitting that a thoroughly representative Exhibition should be held in the metropolis.

This is the first Exhibition that has been devoted exclusively to engineering chemistry, and it will not only help to popularise a comparatively new industry, but by enabling manufacturers to bring their wares to the notice of those actively interested in the science will certainly bring increased prosperity to the chemical trade. The organisers of the Exhibition have done well in upholding the dignity of the science by excluding side shows and popular entertainments, and the educational value is greatly enhanced by the following series of lectures and demonstrations given, or to be given, each evening:—

Monday, May 15. "Modern Methods of Water Purification," Dr. Samuel Rideal, D.Sc., F.I.C.

Tuesday, May 16. "Beetroot Sugar," by The Rt. Hon. The Earl of Denbigh, M V.O.

Wednesday, May 17. "Artificial Silks and Fibres," by Dr. W. P. Dreaper, F.I.C. (under the auspices of the London Section of the Society of Dyers and Colourists).

Thursday, May 18. "Protection of Structural Iron and Steel," by J. Cruickshank Smith, B.Sc., F.C.S., M.S.C.I. (nominated by the Paint and Varnish Society.

Friday, May 19, at 4.30 p.m. "India Rubber," by Dr. H. P. Stevens and Clayton Beadle, F.R.Met.Soc.

Saturday, May 20, at 8 p.m., "Gas Producers," by J. A. Weil.

Monday, May 22, at 4.30 p.m. "Industrial Spirit," by Thos. Tyrer. At 8 p.m., "Progress in Modern Illuminants and their Industrial Application," by Leon Gaster.

Tuesday, May 23, at 8 p.m. "Paper and Pulp," by R. W. Sindall, F.C.S.

Wednesday, May 24, at 8 p.m. "Chemistry of Lithography," by Chas. Harrap.

Thursday, May 25, at 8 p.m. "Sewage Disposal," by W. J. Dibdin.

Friday, May 26, at 8 p.m. "Artificial Production of Precious Stones," by Noel Heaton, B.Sc., F.C.S.

Saturday, May 27, at 8 p.m. "Applications of Electrochemistry and Electro-metallurgy," by Dr. F. Mollwo Perkin (nominated by the Faraday Society).

The Exhibition was formally opened on Saturday, the 13th, by the Right Hon. The Earl of Denbigh, M.V.O., and at a luncheon which followed the opening ceremony several speeches were made by prominent workers in Applied Chemistry.

The President, Prof. Raphael Meldola, F.R.S., proposed the "Health of the King," and Prof. Beilby, F.R.S., in proposing success to the undertaking, briefly explained the object of the Exhibition. Engineering chemistry as an industry had only come into existence within the past twenty years, and this first attempt to demonstrate to the public the important part that chemistry plays in the commerce of this country can only be looked upon as a commencement of a series of increasingly important functions of a similar character.

Mr. Walter Reid, F.I.C., while fully recognising the value of the orthodox college course of chemistry, was of the opinion that not one-tenth of a per cent of the students were able to apply their knowledge to the practice of commercial chemistry. In large chemical operations the chemist and the engineer had to go hand-in-hand, neither could do without the other. This principle was fully exemplified in the now successful manufacture of nitrates from atmospheric nitrogen; the engineer devised and produced the necessary machinery, and the chemist had to work with him to watch and determine the efficiency of the process.

Prof. Sir Edward Thorpe, F.R.S., referred to the "student of Applied Chemistry" as a mythical person who at the present moment existed in essence only. At the Imperial College of Science and Technology they were trying hard to hasten his evolution, but there were many difficulties in the way, and doubtless many mistakes had been made and would yet be made, but success was bound to come eventually.

Dr. Keane, of Sir John Cass Technical Institute, as a representative of that "mythical person" the student of Applied Chemistry, emphasised the importance of thorough technical training; the student should be induced to realise the "responsibility of work."

The Right Hon. The Earl of Denbigh, M.V.O., spoke of the importance of technical chemistry and British industry, and detailed the efforts that had been made to introduce the manufacture of beet-root sugar into this country. Hitherto the chief difficulty had been the fact that it was necessary to commence operations upon a very large scale indeed, involving a large outlay of capital, to insure commercial success, but he suggested that a start might well be made by the preparation of crude beet syrup, which was a valuable product. Small factories for producing this syrup were working successfully abroad and paying handsomely, and there was no reason why they should not do equally well in England.

Considering that this is the first attempt to organise an Exhibition to represent a comparatively new industry the number as well as the character of the exhibits is very satisfactory, and there is little doubt that similar occasions in future will show a great advance. The Exhibition is well worthy of a visit by any who are interested in Chemical Technology, and the lectures are of such a character that they cannot fail to be of interest to the general public and of value to the embryonic "student of Applied Chemistry."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 4th, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Motor Localisation in the Brain of the Gibbon, Correlated with a Histological Examination.*" By Dr. F. W. Mott, F.R.S., Edgar Schuster, and Prof. C. S. Sherrington, F.R.S.

"*Some Phenomena of Regeneration in Sycon, with a Note on the Structure of its Collar-cells.*" By J. S. Huxley.

Production of Normal Individuals from Isolated Cells (as in Wilson's Experiments on Monaxonida).—Cells were obtained singly by straining sponges through gauze. They first unite into lumps, all the kinds being confusedly mixed (Reunion). Next the dermal cells migrated to the surface to form a flat epithelium round a mass of quiescent collar-cells (Reorganisation). Then came Redevelopment: spicules arise, monaxons before triradiates; gastral cavity and osculum appear. The spicules form later than in the larva (where, however, they are certainly precocious), and the regenerates failed to fix permanently. Otherwise Redevelopment resembled normal post-larval development. None became heterocœlous, though one lived and grew as a functioning sponge for several weeks.

The fate of the cells here is *not* a function of their position, for they have to migrate into position before development can proceed.

"*Cancerous Ancestry and the Incidence of Cancer in Mice.*" By J. A. Murray, M.D., Imperial Cancer Research Fund.

The present paper is in continuation of a previous communication (*Roy. Soc. Proc.*, B, 1909, lxxxi., 310). The analysis of the ancestry of 1600 mice bred in the laboratory has permitted their classification in two groups, differing considerably in the incidence of cancer. Out of a total of 562 female mice which lived for six months or more, cancer had occurred in the mother, one or other grandmother, or all three in 340, and in them 62 developed cancer of the mamma (18·2 per cent). In the remaining 222 mice in which cancer was absent from the maternal and grandmaternal ancestors only 19 developed cancer of the mamma (8·6 per cent). The group with recent cancerous ancestry is found on analysis to be more severely attacked at all age-periods than the non-cancerous group (cancerous ancestors remote). Detailed analysis of the ancestors enhances the importance of the differences. The differences exceed their standard errors sufficiently to render them significant. The predisposition is apparently not constitutional, but local, and is regarded as only one of the factors in the development of cancer.

"*Immunisation by means of Bacterial Endotoxins.*" By R. Tanner Hewlett, M.D.

The action of bacterial endotoxins in immunising against the corresponding living organisms has been investigated. Guinea-pigs were the animals employed.

Typhoid Endotoxin.—Series of guinea-pigs were given single injections of the endotoxin, ranging from 0·01 mgrm. to 1·0 mgrm. Five to eleven weeks later the animals were injected with living typhoid culture; considerable protection was obtained, particularly with doses of 0·1 and 1·0 mgrm. The protection afforded by the endotoxin was better, and lasted longer than that conferred by a bacillary typhoid vaccine.

Cholera Endotoxin.—Six guinea-pigs each received 0·25 mgrm. of the endotoxin, and all survived an injection of living cholera culture given eleven weeks later.

Diptheria and *Plague Endotoxins* similarly confer some protection against the living organisms.

No immunising substance was obtained from the *Trypanosoma brucei*.

The results suggest that bacterial endotoxins may be of considerable value as protective vaccines.

The endotoxin solutions maintain their activity for some weeks at least, probably for a much longer period.

A few inoculations of typhoid and diphtheria endotoxins have been performed in the human subject. The inoculations cause some local reaction at the site of inoculation, but little general reaction.

(The endotoxin solutions were prepared by the method described in *Roy. Soc. Proc.*, B, 1909, lxxxi., 325).

"*Method of Disintegrating Bacterial and other Organic Cells.*" By J. E. Barnard and R. T. Hewlett, M.D.

Bacterial toxins are of two kinds, extra-cellular and intra-cellular. The former are excreted into the medium, *e.g.*, beef broth, on which the organism is cultivated, so that by a process of filtration the organisms can be removed, and the toxin is obtained in the filtrate; but the majority of pathogenic micro-organisms do not excrete their toxins, at least to any extent, and the toxins are retained within, and form integral parts of the cells of the organisms.

One method of obtaining these toxins is to mechanically disintegrate the bacterial cell, so that the cell contents are expressed, and the apparatus here described accomplishes this. It consists essentially of a containing vessel, in which, by a suitable rotation of steel balls, the organisms are crushed. The principal conditions to be fulfilled in such an appliance are:—Approximately every cell should be brought under the grinding action. Little or no rise of temperature should take place. The disintegration must be carried out in a vessel which is sealed, so that, when dealing with pathogenic organisms, none can escape at any stage of the process.

These conditions are, in the main, complied with in the apparatus described. Experiments indicate that by this method the cell-juices are obtained unaltered, and suitable for investigations on the chemical composition and properties of the bacterial proteins and other cell constituents. Also that, after the grinding process has been carried on for a sufficient time, practically no cells remain which can be properly stained by any recognised bacteriological method, and which therefore can be regarded as whole cells containing a normal quantity of cell-juice.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 3rd, 1911.

Mr. E. W. Voelcker, President, in the Chair.

Messrs. Horace G. Battye, George Davidson Elsdon, Norman Evers, and Arthur William Knapp were elected members of the Society.

A certificate was read for the first time in favour of Mr. Horace C. Huish, 26, Westbourne Park Villas, Bayswater, W.

A certificate was read for the second time in favour of Mr. Alfred Douglas Heywood.

The following papers were read and discussed:—

"*Evaluation of certain Spices used in Veterinary Medicines.*" By JOHN C. UMNEY and CHARLES T. BENNETT.

The authors deal with the nature of some of the spices used in veterinary medicines, and call attention to the very low grade of many samples of these, and to the desirability of some effective control being placed upon the sale of exhausted or partially exhausted fruits, as well as those adulterated with mineral matter.

"*Detection of Traces of Hydrogen Cyanide.*" By G. D. LANDER and A. E. WALDEN.

A comparison has been made of the delicacy of the Prussian blue as compared with the picrate test for hydrogen cyanide, from which it appears that the former is of at least equal delicacy to the latter.

By evaporating the alkaline cyanide solution to almost complete dryness, adding 2 per cent ferrous sulphate, leaving *in the cold* for ten minutes and acidification, evidence of the presence of 0·000002 grm. of HCN may be obtained. The ferrocyanide reaction may be used for the detection of hydrogen cyanide in the blood and brain of poisoned animals with equal efficiency to the picrate method as applied to the same purpose by Waller.

"*Composition of Blaud's Pills.*" By ALBERT E. PARKES and JOHN D. ROBERTS.

The analysis is given of twenty-eight samples of Blaud's pills, and the variations from the formula of the British Pharmacopœia noted.

"'*Pearl Coating*' *of Pills.*" By ALBERT E. PARKES and JOHN D. ROBERTS.

The pills which were the subject of the previous note were mostly pearl coated. In the present note attention is called to the amount and composition of this coating.

"*A Reaction for Caulophyllin.*" By J. F. H. GILBARD.

The author described a new and characteristic reaction for caulophyllin, the dry resin obtained from *Caulophyllum thalictroides*.

NOTICES OF BOOKS.

Alchemy: Ancient and Modern. By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S. London: William Rider and Son, Ltd. 1911. (4s. 6d. net).

THIS book contains an account of the alchemistical doctrines and of their relations to mysticism and also to modern discoveries in physical science; the author, who has made a study of mysticism as well as of chemistry, believes that there is a certain resemblance between the views regarding the nature and origin of the chemical elements which scientific men are beginning to adopt and alchemistical theories of the physical universe. The book contains short biographies of the greatest of the alchemists and quotations from their works, and is enriched with interesting reproductions of old portrait engravings and other illustrations from works in the British Museum collection and elsewhere.

The Explosibility of Coal Dust. By GEORGE S. RICE. Washington: Government Printing Office. 1910.

THE object of this Bulletin is to present to mine owners and managers a preliminary study of the problem of the explosibility of coal dust, and methods of preventing explosions. It reviews the question from an historical point of view, firstly in Europe, and secondly in the United States, giving a summary of the reports of the various committees appointed to enquire into the problem, and then proceeds to describe experiments in which the conditions of propagation were investigated. The authors give short statements of some provisional conclusions that the work which has already been done has established, but the Bulletin has perhaps a greater value as pointing out the lines of further necessary work. Full accounts are given in it of methods of research on a small scale, and excellent illustrations are provided of the apparatus used in laboratory work; the success of some special preventive measures is discussed, the use of exhaust steam being specially fully treated, and the book concludes with an excellent chronological bibliography.

MISCELLANEOUS.

Nitrification by Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—Both pure oxygen and the nitrogen of the air convert aqueous solutions of ammonia into nitrites under the action of the ultra-violet rays; ammoniacal salts are similarly converted into nitrites as well as aqueous solutions of nitrogenous organic substances. Nitric compounds also yield nitrites, and a concentrated solution of ammonium nitrite is decomposed by the ultra-violet rays giving pure nitrogen.—*Comptes, Rendus*, clii., No. 9.

General Discussion on High Temperatures.—The Faraday Society will hold a General Discussion on High Temperatures on Tuesday, May 23rd, at 8 p.m., at the Institution of Electrical Engineers, Victoria Embankment, W.C. The following programme has been arranged:—Dr. Arthur L. Day, of the Carnegie Institute, Washington, will read a paper on "Recent Advances in Gas Thermometry"; Dr. J. A. Harker, F.R.S., will describe the High Temperature Equipment at the National Physical Laboratory"; Mr. H. C. Greenwood, M.Sc., will read a note on "Boiling-points of Metals"; and Mr. A. Blackie will speak on "The Behaviour of Silica at High Temperatures." Contributions to the Discussion have been promised by Prof. Bodenstein "On the Maintenance of Constant High Temperatures;" M. Féry, "On Stellar Pyrometry"; and others. Dr. R. T. Glazebrook, F.R.S., Director of the National Physical Laboratory, will preside. During the afternoon of May 23rd the Society, by the kind invitation of the Director, will visit the National Physical Laboratory to inspect the high temperature equipment of the laboratory. Experimental demonstrations will be arranged by Dr. Harker and Mr. Greenwood in connection with their contributions to the general discussion. It may be possible to invite a limited number of non-members to visit the Laboratory. Those desirous of taking advantage of this, or of being present at the Discussion in the evening, are asked to communicate with the Secretary of the Faraday Society, 82, Victoria Street, Westminster, London, S.W.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Royal Society of Arts, 8. (Cantor Lecture). "Rock Crystal, its Structure and Uses," by Dr. A. E. H. Tutton.

TUESDAY, 23rd.—Royal Institution, 3. "The Brain and the Hand," by Prof. F. W. Mott, M.D., &c.

— Faraday Society, 8. "Recent Advances in Gas Thermometry," by A. L. Day. "High Temperature Equipment at the National Physical Laboratory," by J. A. Harker. "Boiling-points of Metals," by H. C. Greenwood. "Behaviour of Silica at High Temperatures," by A. Blackie. "Maintenance of Constant High Temperatures," by Prof. Bodenstein (Hanover). "Stellar Pyrometry," by M. Féry (Paris).

WEDNESDAY, 24th.—Royal Society of Arts, 8. "Architecture in America," by Frank M. Andrews (New York).

THURSDAY, 25th.—Royal Institution, 3. "Air and the Flying Machine—Conditions of Safety for Floaters and Fliers," by Dr. W. N. Shaw, F.R.S., &c.

— Royal Society of Arts, 4.30. "The N.W.F. Province of India," by W. R. H. Merk, I.C.S.

— Royal Society. "Experiments on the Compression of Liquids at High Pressures," by the Hon. C. A. Parsons and S. S. Cook. "Optical Method of Measuring Vapour Pressures—Vapour Pressure and apparent Superheating of Solid Bromine," by C. and Mrs. M. Cuthbertson. "Vacuum-tube Spectra of Mercury," by F. Horton. "Production of Characteristic Rontgen Radiations," by R. Whiddington.

FRIDAY 26th.—Royal Institution, 9. "The Greek Chorus as an Art Form," by Prof. Gilbert Murray, M.A., &c.

— Physical Society, 3. Visit to the National Physical Laboratory, Bushy House, Teddington.

SATURDAY, 27th.—Royal Institution, 3. "Phases of Bird Life—Migration," by W. P. Pycraft, F.Z.S.

THE CHEMICAL NEWS.

Vol. CIII., No. 2687.

ON THE PERIODIC TIMES OF SATURN'S RINGS.*

By HENRY WILDE, D.Sc., D.C.L., F.R.S.

In the paper on the "Origin of Saturn's Rings" read by the author last year a new determination was made of the periodic times of the rings based on the commonly accepted distance of Mimas, 3·36 Saturnian units, from observations made by Herschel and subsequently adopted by all astronomical writers. Recent observations of American astronomers with more powerful telescopes, and under more favourable conditions, have reduced the distance of Mimas to 3·16 units, with the consequent increase in the times of rotation of the rings. The difference between the older and later determinations is sufficiently large to induce the author to place on record the results computed from both observations and Kepler's third law. The later result shows for the outermost circumference of the outer ring a periodic time of fourteen hours four minutes, and for the inner edge of the dusky ring a period of five hours forty-five minutes.

That the rings are ejectamenta from the interior of Saturn is further evident from the fact that no causal connection subsists between their times of rotation and that of the planet itself; as the period of the dusky ring is little more than half the time of Saturn's rotation, ten hours thirteen minutes.

The same conclusion may also be drawn with reference to the origin of the two satellites of Mars, as Phobos has a period of only seven hours thirty-nine minutes, while the axial rotation of the planet is twenty-four hours thirty-seven minutes. The comparative minuteness of these bodies, which are estimated to be less than ten miles in diameter, indicates them as ejectamenta rather than the successive condensations of a nebular substance surrounding the planet.

Saturn's dusky ring and the inner satellite of Mars are the only bodies in the solar system that revolve in a shorter time than their primaries.

NOTE ON THE CATALYTIC ACTION OF COPPER OXIDE.

By JAMES STRACHAN.

Meunier (*Comptes Rendus*, 1911, clii., 194) has recently described the flameless combustion of gas mixed with air in a Bunsen burner, on the surface of a copper wire, heated to redness, and immersed in the mixed gases within the tube of the burner.

More than a year ago the same kind of action was observed in this laboratory with a Barthol spirit Bunsen. In the latter a fine jet of methylated spirit vapour is directed against a circle of brass wire-gauze in the Bunsen tube. Air is admitted to the tube below the gauze circle, and the spirit vapour mixed with air is burned above the gauze at the mouth of the Bunsen. When the gauze circle has been in use for several months it has to be renewed, because it becomes oxidised, and when in this state the action of the Bunsen is interfered with by surface-combustion on the gauze. This surface-combustion does not take place with a new gauze, but only when the copper of the brass wire is oxidised superficially. The gauze is uniformly red-hot during the surface-combustion, and the Bunsen flame may be extinguished, when the gauze will continue to glow as long as the mixture of spirit-vapour and air impinges against it. This surface-combustion commences at a comparatively low temperature, as may be shown by shutting off the spirit-vapour and allowing the gauze to cool for a few seconds. When the vapour is turned on again the surface-combustion gradually commences. At first only small areas of the gauze become red-hot, viz., the most oxidised portions; but in a short time the whole circle glows with a bright red heat. The alcohol is burned incompletely by the surface-combustion, and the characteristic smell of aldehyde becomes unbearable when the action is allowed to go on for some time.

It is clearly a case of catalytic action due to rapidly occurring alternations of oxidation and reduction in the surface film of oxide of copper. Sabatier (*Comptes Rendus*, 1909, cxlviii., 26) has shown that the reduction of copper oxide takes place with methyl-alcohol at temperatures below 400° C.

An interesting lecture experiment illustrating this catalytic action of copper oxide may be performed as follows:—A bundle of asbestos fibres is attached to the end of a thin iron wire. The asbestos is then dipped into a strong solution of copper sulphate, and ignited in the Bunsen flame. This operation is repeated, and the asbestos is thus covered with finely divided black oxide of copper. When this is heated and immersed in the gases issuing from a Bunsen burner, the asbestos becomes red-hot and continues to glow. By careful regulation of the air supply the gases may be ignited, but this appears to depend upon the composition of the gas. When the hot asbestos is introduced into the neck of a small conical flask in which hydrogen is being generated from zinc and sulphuric acid, the mixture of air and hydrogen is rapidly ignited. The finely divided copper oxide on the asbestos will also inflame an explosive mixture of hydrogen and oxygen, but as in the previous experiments the asbestos must first be heated in a Bunsen flame, and quickly withdrawn from the latter and introduced into the vessel containing the mixed gases before it becomes too cold.

These lecture experiments may be varied by holding the hot cupricised asbestos above the mouth of a small flask, in which methyl-alcohol is boiling gently. When held at a short distance above the mouth of the flask the hot asbestos rapidly becomes bright red-hot, and the aldehyde smell is at once recognised. By lowering the glowing asbestos into the mouth of the flask the glow ceases, and the copper oxide is reduced to bright metallic copper. By using a bunch of asbestos fibres about 5 cm. long in this experiment, bright metallic copper, red cuprous oxide, and black cupric oxide gradually passing into each other may be produced upon the same length of asbestos. For demonstration purposes the Cu_2O, CuO, and Cu may be successively removed from the asbestos by treating it with ammonia, hot dilute HCl, and HNO_3. The oxidation of organic substances by copper oxide is illustrated also in the case of dendritic growths of copper oxide in paper. At the present time I am working at the chemistry of these growths, but it may be here stated that the mutual catalytic action of cellulose and copper oxide is one factor in their growth. The cellulose is oxidised and tendered, and chemical actions which take place, under ordinary circumstances only with application of heat, occur at normal atmospheric temperatures in the pores of the cellulose.

The catalytic action of copper oxides on mixtures of explosive gases raises another point, which appears to be worth investigation. As pointed out by Sabatier (*loc. cit.*), other metallic oxides have the same property. The experiments described in this paper with asbestos and copper sulphate may be to a great extent repeated, using ferric chloride in place of the latter. The oxide of iron does not appear to be quite as active as the copper oxide however. When we consider the fairly low temperatures at which the action commences and the rapidity with which it progresses when once started, it appears possible that this may be a source of danger in the case of a miner's safety lamp

* Abstract of a Paper read before the Manchester Literary and Philosophical Society.

in which the gauze has become more or less oxidised through long use. Iron-wire gauze is generally used in these lamps, and in a lamp sent me by the manager of a Welsh colliery the temperature of the upper portion of the gauze was found to reach a maximum of 202° C. with a normal flame about 3 cm. high. With the lamp burning too high much higher temperatures were reached, approaching 300° C. In the case of a lamp burning too high, or of the flame impinging even for a short space of time against the gauze, it appears within the bounds of possibility that catalytic action would commence in the presence of an explosive mixture and thus ignite the latter.

Chemical Laboratory.
Ballyclare, Co. Antrim.

THE RARE GASES OF THE ATMOSPHERE.*

By Prof. R. B. MOORE, Butler College, Indianapolis, Ind.

IT is a curious fact that during the thirty or forty years immediately preceding the discovery of argon very little work was done by chemists on the atmosphere. They seemed to feel that here at least an end had been reached, and the wise man would bend his energies in other directions. No suspicion was entertained that the air was a veritable gold mine for chemical research, and even after the evidence seemed to indicate that we had not yet found out all there was to know about our atmosphere, there was a feeling of doubt and uncertainty that made the work move but slowly.

The first clue to the undiscovered elements was partly accidental. In 1882, and several succeeding years, Lord Rayleigh worked on the relative densities of hydrogen and oxygen. In 1893 he published his results on the densities of some other gases, notably those of oxygen, nitrogen, and air. He prepared the oxygen and nitrogen by different methods, and whilst the density of oxygen proved in all cases to be the same, that of nitrogen prepared by chemical methods differed from that of nitrogen obtained from the air. The latter was about 0·5 per cent heavier than the former. A difference of this magnitude could not be accounted for on the basis of experimental error, and the riddle remained unanswered for some time.

Finally, Prof. (now Sir William) Ramsay asked permission of Lord Rayleigh to take up the matter from the chemical standpoint. He had already in some previous work found that red-hot magnesium was a good absorbent for nitrogen. He concluded that if there was any part of atmospheric nitrogen different from the rest a separation might be made by passing the gas over the heated metal. This was tried, the oxygen first being removed by metallic copper. A slight increase in the density of the product was observed. Arrangements were now made to circulate the gas backwards and forwards over the heated magnesium. After several days of this treatment the density was found to be 16·1. At this stage Ramsay did not know that he had to deal with a new element, but thought that the results were due to a triatomic form of nitrogen corresponding to ozone. A further absorption by magnesium finally gave a gas with density about 20. It was only when the spectrum of this product was examined that Ramsay became convinced that he had found a new element.

Meanwhile, Lord Rayleigh was dealing with the problem in a different manner. He passed sparks through a mixture of atmospheric nitrogen and oxygen in the presence of a solution of sodium hydroxide. The hydroxide absorbed the oxides of nitrogen formed, and after removal of the excess of oxygen the resulting gas showed an increased density. From this point Ramsay and Rayleigh continued the work together, and announced the discovery of the new element at the British Association meeting in 1894.

In 1908 the writer was at a dinner in London given to Sir William Ramsay. Lord Rayleigh responded to the principal toast on that occasion, and in his speech most emphatically gave the main share of the credit for the discovery of argon to Ramsay. Whilst this was only just, it goes to show the good feeling which exists between these two notable scientists. Whilst Ramsay deserves the lion's share for the achievement, the work of Rayleigh must not be forgotten.

Ramsay improved on his first method for making argon by using a mixture of lime and powdered magnesium instead of the latter metal alone. The absorption of nitrogen by magnesium is a very slow process, but when mixed with lime the absorption is rapid and complete. The air is first passed over soda-lime and phosphorus pentoxide, and then through a copper tube in which the oxygen is absorbed. From this it goes through the magnesium-lime mixture, over heated copper oxide, and finally through other soda-lime and pentoxide tubes. In order to have the absorption complete some care is required. First, the apparatus must be completely exhausted, and must remain air-tight. Connections may be made by antimony pressure tubing of small bore. The black and grey rubber do not stick tightly at the joints, and the apparatus is sure to leak. It is better to make glass joints wherever possible, and reserve the rubber for connections with the hard glass tubes. The lime must be as free from carbonate as possible, and, of course, perfectly dry. Before the air is passed through it the magnesium-lime tube is strongly heated, and soon turns black owing to the glass being attacked by the magnesium. During this process carbon monoxide and hydrogen are formed in considerable quantities, the first by the reduction of the carbon dioxide obtained from the traces of carbonate in the lime, and the second from the action of water-vapour on the magnesium. These gases should be pumped off as fast as formed, and when the evolution is practically finished air is slowly admitted to the apparatus. Traces of carbon monoxide and hydrogen formed during the actual experiment are oxidised by the copper oxide, and the products absorbed by the soda-lime and pentoxide tubes. When the nitrogen reaches the magnesium-lime tube absorption is indicated by a sudden rise in temperature and the formation of a glowing ring at the rear end of the tube. Unless this ring is formed absorption is not taking place. The glow gradually moves down the tube as the magnesium is used up, making it very easy to know when to stop the experiment.

If the apparatus leaks small traces of air may be removed from the argon by sparking with oxygen in presence of caustic soda. The excess of oxygen is then removed by means of phosphorus.

The amount of labour necessary to make argon in quantity by this method is considerable. The copper-tube finally used by Ramsay was an iron-tube about 6 feet long and nearly 3 inches in diameter. The exhaustion of an apparatus on this scale and the reduction of the copper oxide to copper again all involved a great deal of work; but the final result was 15 litres of argon, which made possible the discovery of the other gases.

Claude has improved on this process to some extent by using the gas obtained from liquid oxygen after the nitrogen has boiled off. Such a gas contains about 3 per cent of argon, whilst air has only a little more than 1 per cent. The amount of nitrogen is low, only about 5 per cent, which also adds to the facility of the preparation. The fractionation of the liquid air must not be allowed to go too far, otherwise the proportion of argon in the liquid oxygen will tend to decrease.

Fisher and Ringe pass air over a mixture of 90 per cent calcium carbide and 10 per cent calcium chloride, heated to 800° C. In this case the temperature is too high for glass and iron tubes must be used. With a properly prepared apparatus considerable quantities of argon may readily be made. The nitrogen and carbide give carbon

* Presented with elaborate demonstrations before the New York Section of the American Chemical Society at an Extraordinary Meeting, March 17th, 1911.

and cyanamide. The oxygen gives lime and carbon, whilst carbon dioxide and monoxide formed at the same time react with the carbide to give carbon.

After the discovery of argon, Ramsay looked for other sources of the element. He heard that Dr. Hillebrand, of the U.S. Geological Survey, had obtained a considerable quantity of nitrogen by heating a mineral called cleveite. Ramsay suspected that the "nitrogen" might be argon, and so obtained a sample of the mineral, heated it with sulphuric acid, pumped off the evolved gas, sparked it with oxygen, and finally ran it into a spectrum tube. The spectrum was entirely different from that of argon, having as a chief characteristic a bright yellow line. According to Ramsay's own account to the writer his surprise was so great that he at first thought there was something wrong with the spectroscope, and took out his handkerchief and wiped the lenses. In this manner terrestrial helium was discovered.

It was now probable that other gases besides helium and argon existed. After a large number of minerals had been examined, in addition to the gases from mineral waters as well as sea-water, Ramsay, assisted by Travers, decided on the fractionation of a considerable quantity of argon. Fifteen litres of the gas as already described was prepared for this purpose. Before this was fractionated, however, a litre of liquid air, presented by Dr. Hampson, was allowed to evaporate, and the last fraction of gas collected separately. The spectrum of this gas, after purification from nitrogen and oxygen, showed a bright green and a bright yellow line not belonging to the argon spectrum. The density of the sample was also greater than that of argon. The new element was called "krypton."

The work was now carried on with great eagerness, for there was promise of still more to come. After the discovery of all the gases and during the examination of their properties, work was continued night and day, only such rest being taken as was absolutely necessary. Such a fruitful field was bound to attract competition, but a complete success was finally achieved.

The 15 litres of argon was now fractionated. The first fraction which came off, containing the gases with the lowest boiling-points, was separated and examined. The spectrum showed a large number of brilliant red and yellow lines, and the density of this particular sample was about 15. This new gas was called "neon." An apparatus was now devised in connection with a Hampson liquid air machine, with which the lighter fractions from the liquid air could be reliquefied and refractionated. Finally, a portion was obtained which could not be liquefied even by air boiling under reduced pressure. This proved to consist largely of neon, but also contained helium, proving the existence of the latter gas in the air. All attempts to separate the helium from the neon were futile until the two were fractionated at the temperature of liquid hydrogen. At this temperature the neon solidified, and the helium could be pumped off.

The residues or last fractions, from 30 litres of liquid air, were now used to make more krypton. The majority of the gas consisted of argon. It was carried through a very rigorous course of fractionation, the last fractions showing some new blue lines, and having a density considerably greater than that of krypton. A final fraction gave a density of 64·0 and was considered pure, as there was no trace of krypton lines. This put the new element "xenon" in its correct place in the Periodic Table. The volume of the gas thus obtained was only 3 cc., and all of the physical constants of the gas were afterward found with this small quantity. Only men possessed of the manipulative skill of Ramsay and Travers could have done this. There was a somewhat larger volume of krypton, about 12 cc., and a still larger volume of neon.

In fractionating a mixture of all the rare gases, the helium and neon, which are dissolved in the liquid argon, boil off very readily. They can best be separated by fractionation with liquid hydrogen, as already stated, but a very good separation can also be effected by another method provided the volume of gas is fairly large. Dewar found that charcoal, especially that made from cocoanut shells, at the temperature of liquid air absorbs gases very readily, generally speaking the heavier the gas the better being the absorption. Neon is partially absorbed by the charcoal, helium not at all; therefore this method can be used for separating the two gases. It is evident that it is easier to get fairly pure neon than it is to get pure helium. In the separation of argon from the two heavier gases, the last portions of the argon carry a considerable amount of krypton. This is readily understood when it is known that the vapour pressure of krypton at the temperature of liquid air is 17 mm. It requires therefore a very tedious fractionation to separate these two gases completely. The case of krypton and xenon is somewhat easier. The vapour pressure of the latter gas at the temperature of liquid air is 0·17 mm. If therefore the two are solidified together the krypton may slowly be pumped from the xenon by means of a Töpler mercury pump. The process is slow, as the krypton evaporates slowly, and has to be repeated a number of times. In doing this, Moore found that a stage was finally reached when no more krypton would come off, and yet if the residue, supposedly consisting of pure xenon, were allowed to evaporate, the gas would show the krypton spectrum. In re-solidifying the mixture, more krypton could be pumped off. The solid xenon evidently occludes the krypton, and a new surface is required for a continuance of the fractionation. Rutherford found the same thing when he tried to remove hydrogen from the solidified emanation for the purpose of measuring the volume of the latter gas. It was necessary to vaporise and solidify a second time before all of the hydrogen could be removed from even so small a quantity of solid as was furnished by the emanation at his disposal.

The original densities found for these gases are:—He, 1·98; Ne, 9·97; A, 19·96; Kr, 40·88; Xe, 64. The ratio of specific heat at constant pressure to that at constant volume indicates that all the gases are monatomic. Their atomic weights therefore are:—He, 3·96; Ne, 19·94; A, 39·92; Kr, 81·76; Xe, 128. They therefore fall naturally in the Periodic Table in a group before the alkalis. Argon is the only one which appears to be out of place, its atomic weight being higher than that of potassium. Originally it was thought that argon was probably a mixture, and vigorous efforts were made to separate it into two or more components. One plausible explanation has been advanced—that argon contains a small percentage of diatomic molecules; 5 per cent of such molecules would reduce the density to 19 and the atomic weight to 38. Such a condition is not inconceivable, but if it were a fact the density of the gas would probably vary with the temperature, which is not true. The ratio of the specific heats for argon is 1·659, which closely approximates the theoretical 1·667 for a perfect gas. Five per cent of diatomic molecules should give a ratio of 1·648 instead of 1·659. No satisfactory explanation, therefore, can be advanced at the present time for the anomalous position of argon in the Periodic Table.

More recent atomic weights for all the rare gases are as follows:—He, 3·994; Ne, 20·2 (Watson); A, 39·89 (Fisher and Hehnel); Kr, 83·01; Xe, 130·70 (Moore). Watson and Moore both had larger quantities of gas to work with than was possessed by Ramsay and Travers. Watson, applying the critical constants of krypton and xenon to Moore's figures, has deduced the atomic weights 82·92 and 130·22 for krypton and xenon.

The rare gases have apparently so far resisted all attempts at getting them to combine either with each other or with the other elements. When Ramsay first obtained argon in quantity he used rigorous methods to act on it chemically. It can be sparked with oxygen, chlorine, or hydrogen without success. Red-hot sodium hydroxide, sodium peroxide, or fused potassium nitrate have no action. Fluorine, nascent chlorine, and red-hot magnesium are equally ineffective. Helium appears to be just as inactive as argon. More recently, Fisher and

Schroter have passed an arc discharge between electrodes of different metals immersed in pure liquid argon. Whereas the metals usually underwent a decided change—lithium and sodium becoming brown powders and zinc and calcium changing to black modifications—in no case could it be proved that any compounds had even a momentary existence. And yet there is some evidence that possibly compounds may be formed under certain conditions. Fergusonite is a mineral which, on heating, evolves considerable quantities of helium. In doing so it becomes quite hot; in other words, it is an endothermic mineral. Again, when a discharge is passed between the electrodes of ordinary spectrum tubes containing the rare gases, there is a very decided tendency for the electrodes to "splash" on to the sides of the tubes. This coating absorbs the gas and shortens the life of the tube. This splashing would seem to indicate that end, thermal compounds were momentarily formed. The field seems to have been pretty well worked over in connection with helium and argon. But very little has been done with the other gases on account of their rarity. Neon has now been obtained in quantity by Mr. Claude, who uses a continuous method of fractionation, and finally separates the helium and neon by charcoal and liquid air. Ramsay and Moore possess between them about 250 cc. of xenon and a somewhat smaller quantity of krypton. Ramsay and Gray are at the present time attempting to make a compound with xenon. In a private communication from the former to the writer, he states that when xenon is sparked with hydrogen and then fractionated it has the density obtained by Moore, but if sparked with oxygen and fractionated the density is higher. The results, however, are erratic. There seems to be a compound, but they have been so far unable to isolate it.

As already stated, all of the rare gases are found in our atmosphere. The amount of argon in the air can be estimated without difficulty, but it is impossible to get the same degree of accuracy in the case of the other gases. When such large volumes of air are used there will almost surely be some loss of the rare gas which is to be estimated. There is no doubt, however, that Ramsay's first figures are very near the truth. They are:—

Helium	one part in	245·000	by volume.
Neon	,,	81·000	,,
Argon	,,	106·8	,,
Krypton	,,	20,000,000	,,
Xenon	,,	170,000,000	,,

More recent determinations by Claude on the first two gases give a higher proportion, viz., helium one part in 200,000, and neon one part in 66,000. Claude states that some of the neon was probably lost, so that the quantity may be as large as one part in 60,000. The same observer found one part of hydrogen in 10,000,000 volumes of air.

One interesting thing in connection with these gases is the fact that the spectrum of the aurora borealis is probably entirely due to krypton. The green krypton line shows brightly in the aurora spectrum and at times others of the lines. The aurora is probably formed by the negative particles discharged from the sun which are caught over the equator by the earth's magnetic lines of force, which are horizontal at this point but dip towards the poles. Here, when the particles strike the outer layers of the atmosphere, luminescence is the result. The reason that the krypton spectrum alone is seen is because this spectrum is very persistent. The green and yellow lines can be plainly seen in a spectrum tube when the vacuum is so high that the current will hardly pass. At a height of 70 or 80 miles the pressure of the atmosphere would be such that the krypton spectrum would be apparent, but no other.

Helium is occluded in a large number of minerals; indeed, is contained to a greater or lesser extent in all minerals and rocks. The origin of the gas was explained when Ramsay and Soddy showed that the radium emanation gave rise to helium. The question received still further light when Rutherford and Geiger proved the identity of the α-particle and the helium atom. The helium found in the earth's crust, therefore, is formed by disintegration of radio-active types of matter with the elimination of α-particles. We are indebted to the Hon. R. J. Strutt for most of our knowledge along this line. Generally speaking the amount of helium in a mineral is proportionate to the amount of uranium and thorium present. Strutt has therefore sought to determine by this means the age of minerals and rock deposits with fair success. In some cases, however, the rate of leakage is greater than the rate of formation from radio-active changes.

One mineral, beryl, contains a considerable amount of helium and practically no radio-active matter. Boltwood explains this on the basis that in the crystallisation of the mineral only one of the longer lived products of disintegration, such as radium or ionium, has remained with the mineral. This has decayed with the formation of helium, and, as there was no uranium or thorium present, the mineral became inactive. Strutt finds too much helium in the Stassfurt minerals, sylvine and carnallite, for the uranium present, and suggests potassium as the source of the extra helium. Indeed, the radio-activity of so-called ordinary matter may have a good deal more to do with the accumulation of helium in geological times than we at present suspect. Argon is only found in minerals containing zirconium, although there is no apparent connection between the two. Helium, neon, and argon are all contained in the waters of many springs. Cady and McFarland found helium in forty out of forty-one samples of natural gas examined.

The helium occluded in the minerals may be liberated either by heating or by solution in acids. In the latter case the whole of the gas is set free. A high temperature is required to get rid of all the gas by heating. Some experiments by Wood with monazite showed that very little gas came off at 500° C., and at 900° C. it took twenty-four hours of heating to liberate all the gas. For thorianite, 0·7 per cent came off at 300° C. after five hours heating, 8·5 per cent at 500° after eighty hours, and the whole at 1000° after thirty hours.

The origin of neon, argon, krypton, and xenon is a matter of extreme interest and importance. The fact that helium is continuously being produced during radio-active changes fully accounts for the presence of this gas in our atmosphere and in the earth's crust. The fact does not explain the origin of the other gases, although it is extremely suggestive. The well-known work of Ramsay and Cameron seemed to give a definite answer to the question. They found that if a solution of copper nitrate were treated with radium emanation, not only was lithium found in the solution. but the gas, which was afterwards pumped from the bulb, consisting mostly of hydrogen and oxygen from the decomposition of the water, after proper purification gave the argon spectrum but showed no helium lines. The gas, however, contained 0·34 cc. of nitrogen. When distilled water was treated with the emanation neon with a trace of helium was obtained, but no argon. The "water-gas" contained 0·307 cc. of nitrogen. The contention of Ramsay and Cameron was that, under certain conditions, not only helium but some one of the other rare gases of the atmosphere might constitute one of the disintegration products of the radium emanation. Some experiments of Rutherford afterwards proved that the neon from 1/10 cc. of air could be detected under similar conditions. This might be used as an explanation of the presence of neon in the second experiment, but would not explain the absence of helium and also of neon in the first. The nitrogen in both cases was about the same, and therefore if this were due to a leak helium and neon should have been recognised in both cases. The question remains open for further work when larger quantities of emanation are available.

There is no longer any doubt of the theoretical possibility of transmutation of the heavier to the lighter elements whatever may be said of the reverse process. Even the

possibility of the latter is denied by few. As long ago as 1873 F. W. Clarke showed great foresight when he said: "We do not know but that the evolution of one element from another may be possible." A study of the nebulæ and fixed stars has greatly strengthened this view. The peculiar properties of the rare gases existing as they do in our atmosphere suggests a similar if not a common origin. Rutherford has shown that if the velocity of the α- and β-particles, in radio-active changes, fell below a certain limiting value, we would not be able to recognise them by our present methods; therefore the possibility of all matter, or at least some at present unsuspected matter, being radio-active, must be seriously considered. The radio-activity of potassium and the possible formation of helium from it has already been mentioned. Rubidium also shows a feeble activity. If these things are so they suggest a possible origin for some if not all of the rare gases without any way interfering with our present theories concerning the disintegration process.

As Ramsay only prepared 3 cc. of xenon he did not have enough material for a fractionation in order to look for a still heavier gas of the argon group. Placing hydrogen over lithium in the Periodic Table there would be room for one element lighter than helium. Leaving the radio-active emanations out of consideration there would also be place for two elements heavier than xenon. Watson made a careful search for the lighter gas. He fractionated a considerable quantity of helium and neon obtained from air, and compared the spectra of the different fractions with those of pure helium and neon. The only result was to add a number of lines to the known spectra of these two gases. This was disappointing, for the existence of "nebulium" in the nebulæ and "coronium" in the sun made the existence of such a light element strongly probable. Moore worked on the heavier gases. In order to carry out the search it was necessary to prepare a considerable quantity of xenon and then fractionate it. A start was made with nineteen tons of liquid air. Since xenon at the temperature of liquid air has a vapour pressure of 0·17 mm., and at $=205°$ C. this pressure is only 0·0005 mm., it follows that a new gas with an atomic weight heavier than that of xenon would have a vapour pressure at least not greater than 0·0005 mm. Therefore on allowing liquid air to boil away slowly almost all of such a gas would remain with the dregs of liquid oxygen. The oxygen obtained from the nineteen tons of air was allowed to evaporate into a gas holder. The oxygen was removed from the 2000 litres of gas so obtained by passing over melted phosphorus, the nitrogen in the usual way, with magnesium and lime, and the xenon finally obtained carefully fractionated. The result was negative. A second attempt was made with the residues from 100 tons of air, eliminating almost entirely the use of water during the fractionation. This was advisable as the coefficient of absorption of xenon is 0·2189, and that of the new gas would be higher. The result was again negative. The research, however, proved that if such a gas does exist in the atmosphere the proportion is less than one part in 2,500,000,000.

The relation of the radio-active emanations to the rare gases is a question of interest. Radium, thorium, and actinium all give rise to these active gases, and, assuming that they are heavier than xenon, there is no place for all of them in the Periodic Table. Cameron groups them together and thus gets round the difficulty The remarkable work of Ramsay and Gray in directly weighing the radium emanation, and thus obtaining its density, has probably settled its position in the Table. They used a balance sensitive to 1/250,000th of a milligrm., and the average of five determinations gave 223 as the atomic weight of the gas. They suggest the name *niton* for radium emanation as being more appropriate to the element as a probable member of the argon group. The boiling-point of the emanation ($-71°$ C.) is in fair agreement with the boiling-points of the other five elements, but its melting-point ($-150°$ C.) is not in harmony with the theory that it is one of the argon group. Outside of this, however, its properties would seem to indicate it as the heaviest member of the group.

The work on the rare gases is not by any means complete. Indeed, they are almost as much a mystery to the chemist as when first discovered. Much is yet to be done, notwithstanding the magnificent work of Ramsay and Travers. It may be that the future will hold many surprises for us in connection with this interesting group of elements.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 11th, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Method of Making Visible the Paths of Ionising Particles through a Gas.*" By C. T. R. Wilson, F.R.S.

The paths are made visible by condensing water upon the ions immediately after their liberation, an expansion apparatus being used which works without appreciable stirring up of the air.

The trails of ions formed by the alpha particles from radium have in this way been made visible and photographed, very dense and sharply defined rays of cloud being formed on expansion.

Air exposed to beta rays gives clouds consisting mainly of faint straight threads radiating from the source; these have not yet been photographed.

In air exposed to gamma rays the cloud is again in the form of straight threads traversing the cloud chamber—the tracks of beta particles from the walls.

The cloud formed in air exposed to Röntgen rays is entirely concentrated in minute streaks and patches. A photograph shows these to consist mainly of fine threads not exceeding a few mm. in length, and generally far from straight, probably the tracks of cathode rays produced in the air by the X-rays. The whole of the ionisation would appear, as Bragg has already suggested, to be effected by the cathode rays derived from the X-rays.

"*The Vertical Temperature Distribution in the Atmosphere over England, and some Remarks on the General and Local Circulation.*" By W. H. Dines, F.R.S.

This paper gives an account of the results of some 200 observations made in the British Isles in the year 1908-09-10 on the temperature of the upper air. It discusses the annual variation of the temperature up to 14 kilometres, and shows that the annual range remains fairly steady, with a total amplitude of about 12° C. up to 11 kms., above which the range suddenly drops to 3°, and the times of the maxima and minima go back two months. The question of the daily variation at great heights is then discussed.

The relation between the temperature at various heights and the height of the barometer at the surface is dealt with, and it is shown how over a low-pressure area with the barometer below 740 mm. the temperature of the first 8 kms. is very low, reaching at 7 kms. a value of nearly 10° C. below its average value, and that above 10 kms. it is considerably above the average. In the anti-cyclonic parts the conditions are reversed, and it is warm below and cold above. The height at which the isothermal region is met with in summer and winter and in times of high and low barometer is then referred to. A statement with regard to the existence of similar conditions that have been found to exist on the Continent is also given.

In the second part of the paper various theoretical considerations are taken into account. It is shown that if an extensive and strong wind exists in any part of the atmos

sphere, warm air will be found somewhat below it on its right hand, and cold air above it on the right, with converse conditions on the left; and it is pointed out that this agrees with the distribution of temperature that is found to exist at the various levels of cyclones and anticyclones.

"*Some Mineral Constituents of a Dusty Atmosphere.*" By Prof. W. N. HARTLEY, F.R.S.

"*The Path of an Electron in Combined Radial Magnetic and Electric Fields.*" By H. STANLEY ALLEN, M.A., D.Sc.

The path of an electron in a radial electric field superposed on a radial magnetic field is found to lie on a circular cone whose vertex coincides with the magnetic pole. If the surface of the cone is developed into a plane the trace of the path is a conic section with the vertex as focus. The solution in the particular case in which there is no electric field has been given by Poincaré; the path is then a geodesic line on the surface of the cone, and of course becomes a straight line when the cone is developed. In cases which can be realised experimentally the developed path is hyperbolic, and does not in general differ greatly from a straight line.

An account is given of some experiments carried out to illustrate the theory. The first observations were made with a focus tube in which the anti-cathode was the pole of an electromagnet. The phenomena observed are easily explained in terms of the theory. Other vacuum tubes were prepared in which a fine pencil of cathode rays could be produced by means of a Wehnelt cathode. In a radial magnetic field the stream of electrons assumed a spiral form, and a number of photographs were obtained showing the spiral paths on a cone of revolution.

"*Absolute Measurement of Light—a Proposal for an Ultimate Light Standard.*" By R. A. HOUSTOUN, M.A., Ph.D., D.Sc.

A thermopile cannot be used for the measurement of candle-power because it gives the same value to the energy of every wave-length, invisible as well as visible. The author has, however, found by spectro-photometric investigation in the ultra-violet, visible, and infra-red parts of the spectrum that, if a filter consisting of aqueous solutions of copper sulphate and potassium bichromate in a particular strength in glass cells be placed before the thermopile, then this filter stops the ultra-violet and infra-red entirely, and lets through a fraction of each wave-length in the visible spectrum proportional to its visibility. In other words, it weights each radiation according to its visibility.

The voltage on a tantalum lamp was varied over a wide range, and its candle-power as read by thermopile and filters agreed well with the readings of a photometer. Owing to the high sensitiveness of the galvanometer required the method is not suitable for commercial application, except perhaps for integration photometry when a number of thermopiles might be connected in series with the one galvanometer.

The importance of the method lies in the fact that it provides a satisfactory basis for heterochromatic photometry independent of the Purkinje phenomenon at all intensities. The author therefore proposes to use it for defining the unit of light intensity. He would define the latter as that source, the total intensity of radiation from which at a distance of one metre after passing through his filters would be x ergs/sq. cm., sec. For the standard candle x should be about 0·8.

"*Harmonic Expansions.*" By Prof. A. C. DIXON, F.R.S.

FARADAY SOCIETY.

Ordinary Meeting, May 2nd, 1911.

Mr. JAMES SWINBURNE, F.R.S., President, in the Chair.

Mr. A. SCOTT-HANSEN, C.E., of Christiana, read a paper on "*Hydro-electric Ptants in Norway and their Application to Electrochemical Industry.*"

The reading of the paper was illustrated by means of a large number of beautiful lantern slides, which brought out in a very striking manner the present position of hydro-electric development in Norway.

The physical configuration of Norway is remarkably favourable for the utilisation of the large number of water-falls to be found on the seaboard of the mountain chains which almost cover the country, and through whose valleys the enormous quantity of water precipitated from the western and south-eastern sea breezes finds its way as rivers flowing down to the sea. In the winter the rainfall takes the form of snow, so that the volume of water brought down by the rivers is at its greatest from May to July, when the snows melt on the mountains. To make use of the water-power storage is therefore necessary, and for this the nature of the country is peculiarly adapted, being covered with lakes that have very contracted outlets and which can be easily converted by damming into storage reservoirs. Thus in the watershed of Skien the natural water-power of 50,000 h.p. has been increased to an available horse-power of 375,000, while the Mösvand reservoir has increased the water-power of the Rjukan factories from 30,000 to 250,000 h.p. with a capital outlay of only some £85,000.

The total water-power in Norway has been estimated at from five to seven million horse-power, but as much of the country has not been hydrographically surveyed, this is probably too low an estimate. The power stations can supply power at from 22 to 44 shillings per e.h.p.-year, and in some cases even for less; and as the quantities available are as high as from 50,000 to 100,000 h.p. for a single fall, the conditions are ideal for the development of electrochemical and electrometallurgical industries. Many such industries have already reached an advanced stage of development. Thus nearly 180,000 h.p. will be utilised this year in the manufacture of nitrates of lime, soda, and ammonia from the air by the Birkeland-Eyde process and the Badische Anilin und Sodafabrik Company's process; about 60,000 h.p. are employed in the manufacture of calcium carbide, and other electrochemical and electro-metallurgical industries absorb at present some 20,000 h.p. Now that a suitable electric furnace—the Grönwall—has been designed for the smelting of iron ore, a furnace that has yielded excellent results on a practical scale, electric iron and steel smelting is likely to develop largely in the near future, for Norway possesses extensive deposits of iron ore. Three plants, aggregating 16,000 h.p., with provision for increasing to nearly 60,000, are now being erected at Hardanger, Arendal, and Tinfoss. Other ores, notably, copper, nickel, zinc, will also possibly be electrically smelted at no distant date.

The second portion of the paper describes in some detail the various hydro-electric schemes now being developed in Norway.

On the Glommen River, in the east, three falls are utilised. The uppermost, Kykkelsrud, yields about 40,000 h.p., of which 10,000 kilowatts is transmitted at 60,000 volts (3-phase 50 periods) to Christiana 31 miles away, and the remainder to Sarpsborg. At Sarpsborg occurs the lowest fall of the Glommen, and here there are two power stations—Hafslund, supplying 24,000 h.p. to calcium carbide works and for zinc smelting, and Borregaard, whose output of 26,000 h.p. is utilised by the Kellner Partington Paper Pulp Company, Ltd., owning the largest works in Norway. The intermediate fall on the Glommen is at Vamma, where a dam is now in course of construction under considerable difficulties. This dam will have a height of 90 feet, and will be one of the largest in Europe. The power station will be in the centre of the river bed below the dam and will yield some 70,000 to 80,000 h.p.

A large number of the minor power stations in the south supply the towns with light and power. Among the smaller electrochemical works are the electro-iron and steel works at Arendal, the experimental nitrate works of the Badische Company at Christianssand, and nickel and

aluminium factories near the same town. The nickel works refine nickel matte and turn out about 400 tons of the pure metal per annum. At Gjøssingfjord is Mr. Albert Hiorth's small experimental electro-steel works. At Vadheim, on the west coast, is a sodium factory, and at Trondhjem, in the north, carbide, ferro-chrome, and ferro-silicon are manufactured.

Another great power centre is in the Telemarken district in the south-east of Norway. The Svaelgfoss power station supplies 40,000 h.p. to the nitrate factory at Notodden at a voltage of 10,000, delivered without transformation. The four 10,000-h.p. machines—capable of developing 13,000 h.p.—are among the largest in the world. A power station now being constructed at Lienfoss will be able to furnish Notodden with a further 20,000 h.p. The Tinfoss Works, also at Notodden, are intended to generate 15,000 h.p., to be used mainly for iron and steel smelting.

The third of the great Norwegian falls is the celebrated Rjukanfoss waterfall on the Maaneely River. The Mosvand dam, above this fall, provides a reservoir of about 840 million cubic metres (tons) of water, and five miles below is another dam, forming the intake for the power station, situated 1000 feet below. A lower fall of about 1000 feet provides the power for a second station. Both of these power stations—the largest in Europe—will yield 140,000 h.p., there being in each 10 units of 14,000 h.p. The turbines, on account of the great height of the falls, are Pelton wheels. The construction of the dams, flumes, and power stations at Rjukanfoss was attended with great engineering difficulties, which are described in the paper. The power from these stations is transmitted through sixty copper and aluminium cables to Saaheim, where factories for the manufacture of nitrogenous products to employ from 2000 to 3000 persons are in course of erection.

The paper concludes with a description of the power plant at the Tysse falls, which consists of seven units, each of 4500 h.p., and from which electric energy is transmitted at 12,000 volts to Odda, where it is used for the manufacture of calcium carbide and of cyanamide. Here again, on account of the steep mountainous character of the country, great difficulties presented themselves, particularly in the drilling of tunnels 1320 feet above the fjord, and in fixing the flumes, some against a smooth precipice, with an inclination of 60°. The Tysse power station will eventually yield some 100,000 h.p.

The NORWEGIAN MINISTER (Mr. Vogt) expressed his pleasure at having had the opportunity of hearing Mr. Scott-Hansen describe the wonderful industrial developments now taking place in Norway.

Dr. F. MOLLWO PERKIN pointed out that much of the conservation of natural resources they had heard of that evening, directly benefitting their own country, had been brought about without the destruction of beautiful scenery.

Mr. W. MURRAY MORRISON remarked on the ease with which hydrographical data in Norway were obtainable from the Government. He drew attention to the surprisingly low cost of Norwegian water-power—in some instances it reached 15s. or 16s. per e.h.p.-year, including all capital and running charges. He was glad that Englishmen had been associated with some of these developments, although difficulties were put in the way of attracting capital.

Mr. F. W. HARBORD supplemented some of the information contained in the paper, dwelling particularly on the electrometallurgical processes in operation—namely, the manufacture of iron, equal in quality to the best charcoal iron, and the smelting of zinc. The manufacture of soluble phosphates was likewise a promising industry.

Mr. L. A. SMART remarked on the magnitude of the carbide industry in Norway. As regards iron smelting, the pure magnetic ores found there were particularly suitable for electrical treatment. He hoped that it might be possible to arrange for the Society to hold a Summer meeting in Norway.

Mr. CHARLES WEISS said that propositions were being discussed for electrolytic copper refining in Norway, probably in connection with the electric smelting of the ore. He asked whether the Birkeland-Eyde or the Badische nitrate process were the more economical.

The CHAIRMAN having moved a hearty vote of thanks to the author, Mr. SCOTT-HANSEN replied briefly to the points raised in the discussion. Replying to Mr. Weiss, the relative superiority of the two furnaces could not be decided until experiments now in operation were concluded. The Birkeland-Eyde furnaces could be built in larger units, however; up to 4000 kilowatts each as against 800 in the case of the Badische furnace. Referring to the suggestion of Mr. Smart, he offered a hearty invitation to the Society to come and see with their own eyes the plants he had described.

A paper communicated by Mr. EDGAR STANSFIELD, M.Sc., described "*Two Simple Forms of Gas-pressure Regulators.*" (Will be inserted in full).

A paper by Dr. W. C. MCC. LEWIS, entitled "*Internal, Molecular, or Intrinsic Pressure—a Survey of the various Expressions proposed for its Determination,*" was laid before the meeting and taken as read:—

If we consider an imaginary plane of unit area placed in any direction well inside a liquid mass, equilibrium across this plane is maintained by the balanced attractive and repulsive molecular forces, which we have reason to believe are of very great magnitude, amounting to hundreds or even thousands of atmospheres. The attractive force per unit area is defined as the molecular, internal, or intrinsic pressure of the liquid, and is usually denoted by the symbol K. The present paper is a survey of the various attempts which have been made to estimate the value of K for various liquids. The subject has been investigated for more than a century, the first attempt being that of Thomas Young, in 1805, followed shortly after by Laplace's classical work. In historical sequence, the most important of the later contributions are those of A. Dupré (1864-69), van der Waals (from 1873 onwards), Bakker (from 1888), Milner (1897), Dieterici (1898), Richards (1902), Traube (from 1902), and Benedicks (1905).

According to the theory of Laplace, K may be written as the product of two terms, the first being an integral whose upper limit is the so-called range of molecular attraction; the second being a term involving the square of the density of the substance. This has been generally accepted by all investigators, but the real difficulty comes in on the question of the effect of temperature. Dupré regarded K as independent of temperature, and hence, since the density varies with temperature, the integral term—*i.e.*, the range of molecular attraction—must be a function of temperature. Van der Waals, on the other hand, regarded K as varying with temperature, the Laplace integral being replaced by a quantity a characteristic of the liquid under investigation, and considered in van der Waals' earlier work as a constant independent of temperature. The comparison of experimental results with theoretical has, however, shown this to be only approximately true, and the position taken up at the present time is that both K and a vary with the temperature—*i.e.*, decrease as temperature rises. Thus, although we are able to assign the correct order of magnitude to the numerical values of K, no closer degree of approximation appears as yet to be possible.

It is pointed out in the paper that the problem considered from the thermodynamic standpoint becomes analogous to that of Nernst regarding the quantitative connection between heat change (or total energy change) and the free energy change in a chemical reaction beyond that given by the Gibbs-Helmholtz equation. As some further assumption connecting K and T is required, the author tentatively suggests that the fractional rate of change of K with temperature may be equal to the corresponding change with temperature of the latent heat of vaporisation of unit volume of the liquid. At any rate, this gives results of the same order of magnitude as those of van der Waals.

From the standpoint of thermodynamics the problem develops into one of great interest, namely, the correct treatment of internal work and its relation to total and free energy changes respectively.

CHEMICAL SOCIETY.

Ordinary Meeting, May 4th, 1911.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

Messrs. J. Bate and R. Hurst were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Owen Blackhurst, Downing, Broughton, Preston; Ganesh Datta, B.A., Dera Ismail Khan, N.W.F.P., India; Joges Chandra Ghose, M.A., Bhagalpur, Behar, India; Herbert James Ling, Hankow, China; Felix Gabriel Paul, No. 64, 38th Street, Rangoon, Burma; William Keighley Walton, Beechwood, Upper Rushton Road, Thornbury, Bradford.

The President announced that a general discussion on the subject of "High Temperatures" would take place at a meeting of the Faraday Society to be held on Tuesday, May 23rd, 1911.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—John Ernest Roux Adendorff; Samuel James Manson Auld, D.Sc., Ph.D.; Ernest Carr Bennison; Richard Charles Bowden, B.Sc.; Arthur Stewart Bowyer, M.Sc.; John Eric Collington; Clement Arthur Crook; Cecil Reginald Crymble, B.Sc.; Atulchandra Datta, M.A.; William Henry Dickinson, M.B., Ch.B.; Oliver Statham Douse, B.Sc.; Alfred Thomas Eggington, B.Sc.; Arthur Alfred Eldridge, B.Sc.; Algernon John Elkington; Alfred Walker Empson; Ralph Roscoe Enfield, B.A.; Thomas Grantham Giddy; Henry Francis Harwood, M.Sc., Ph.D.; Edwin Burnhope Hughes; Thomas Riley Lucas; Roney Forshaw Messervy; Oswald Mansell-Moullin, B.A.; Leonard Owen Newton; Idris Larkby Owen, M.Sc.; John Lawrence Robinson Pastfield, B.A.; Richard Garnet Penny; George Arncliffe Percival; Albert Cherbury David Rivett, B.A., B.Sc.; Robert Robison, Ph.D., B.Sc.; Eric Everard Walker; Henry Hough Watson; Alfred Henry Finniss-Wheldon; William Arthur Reginald Wilks, M.A.; William Wood; Robert Wright, M.A.

Of the following papers, those marked * were read:—

*112. "*The Constituents of Bryony-root.*" By Frederick Belding Power and Charles Watson Moore.

The material employed for this investigation consisted of the freshly collected roots of *Bryonia dioica*, Linné.

The roots were found to contain an enzyme, which was obtained in the form of a light brown powder. This product slowly hydrolysed the glucosidic constituent of the root, and also effected the hydrolysis of amygdalin and salicin.

An alcoholic extract of the root, when distilled in steam, yielded a small amount of a pale yellow essential oil. From the portion of the extract which was soluble in water, and contained a quantity of sugar, there were isolated:—(i.) A colourless neutral *substance* (m. p. 220–222°), which appears to possess the formula $C_{20}H_{30}O_5$, and has $[\alpha]_D$ +58·6°); (ii.) an amorphous glucosidic product, having a bitter taste, which, on hydrolysis, yielded a brown resin and a sugar, from which *d*-phenylglucosazone (m. p. 208—210°) was prepared; (iii.) an amorphous alkaloidal principle, possessing an intensely bitter taste, which was apparently incapable of forming any crystalline salt.

The portion of extract which was insoluble in water consisted of a dark brown viscid resin, amounting to about 2 per cent of the weight of dried root employed. From this material the following compounds were isolated:—(i.) A phytosterol, $C_{27}H_{46}O$ (m. p. 137°), which was optically inactive; (ii.) a new dihydric alcohol, *bryonol*, $C_{22}H_{34}O_2(OH)_2$, melting at 210—212°, and yielding a *diacetyl* derivative, melting at 152°. Bryonol belongs to a group of dihydric alcohols possessing the general formula $C_nH_{2n-8}O_4$, which comprises the following additional compounds:—Ipurganol, $C_{21}H_{32}O_2(OH)_2$; grindelol, $C_{23}H_{36}O_2(OH)_2$; and cucurbitol, $C_{24}H_{38}O_2(OH)_2$; (iii.) oleic, linolic, palmitic, and stearic acids.

The activity of the root appears to reside chiefly in its resinous and alkaloidal constituents, and the so-called "bryonin" of previous investigators has been shown to consist of a complex mixture, which was not entirely glucosidic.

*113. "*Reactivity of the Halogens in Organic Compounds.* Part VI. *The Mechanism of Negative Catalysis.*" By George Senter and Alfred William Porter.

The kinetics of the reaction of silver nitrate with bromoacetic and α-bromopropionic acids respectively in absolute ethyl alcohol have been measured at 49·9°. The reactions are retarded by nitric acid to an even greater extent than in aqueous solution. A formula which represents the results fairly satisfactorily was given.

A formula which represents accurately the decomposition of α-bromopropionic acid by water has been derived on the assumption that both the anions and the non-ionised acid react with water.

It was shown that the usual formula which represents negative catalysis as a difference between two factors is not in accord with the available experimental data. An empirical formula, based on the assumption that the rate of reaction is inversely proportional to the concentration of the negative catalyst, was shown to represent the experimental results very closely. The mode in which accurate formulæ representing negative catalysis may be derived was indicated, and the connection between the accurate and the empirical formula pointed out.

*114. "*The Constitution of Scopoletin.*" By Charles Watson Moore.

Scopoletin, a fluorescent substance obtained from *Scopolia japonica* and several other plants, has been shown to be 4-hydroxy-5-methoxycoumarin, since by prolonged boiling with aqueous potassium hydroxide it is converted into 2:4-dihydroxyanisole. When, however, the alkali hydroxide is allowed to act for a few minutes only on scopoletin, 2:4-*dihydroxy*-5-*methoxycinnamic acid* is formed. In connection with the investigation, the following compounds have also been prepared and characterised:—2:4-*Diacetoxyanisole* (m. p. 62—64°); 2:5-*diacetoxyanisole* (m. p. 94°); 2:4:5-*trimethoxycinnamic acid* (m. p. 163—165°); 2:4-*dihydroxy*-5-*methoxy*-β-*phenylpropionic acid* (m. p. 69°); the *lactone* of 2:4-*dihydroxy*-5-*methoxy*-β-*phenylpropionic acid* (m. p. 155°); the *lactone* of 2-*hydroxy*-4-*acetoxy*-5-*methoxy*-β-*phenylpropionic acid* (m. p. 135°); 2:4:5-*trimethoxy*-β-*phenylpropionic acid* (m. p. 96°); and *methyl* 2:4:5-*trimethoxy*-β-*phenylpropionate* (m. p. 54°).

115. "*Note on the Action of Hydrogen Dioxide on Thiobenzanilide.*" By Harold Leete and Edward de Barry Barnett.

It has been shown previously (Jacobson, *Ber.*, 1886, xix., 1068) that 1-phenylbenzothiazole is produced when thiobenzanilide is oxidised in alkaline solution with potassium ferricyanide. The authors now find that when the oxidation is brought about by hydrogen dioxide in alkaline solution, sulphur is eliminated as sulphuric acid, and benzanilide is formed. In neutral solution, however, a compound, $C_{13}H_{11}ONS$, is also formed, and this is the sole product when the oxidation takes place in acid solution. As a similar product is not obtained from benzanilide,

it would seem that the oxygen is taken up by the sulphur atom, and this receives confirmation from the insolubility of the substance in alkali. No sulphinic acid appears to be formed, as is the case when hydrogen dioxide acts on thiocarbamide in neutral or alkaline solution (Barnett, *Trans.*, 1910, xcvii., 63). In order to bring about the oxidation, the thiobenzanilide (20 grms.) was dissolved in alcohol or acetone, a few cc. of dilute sulphuric acid added, and then 20 grms. of a 30 per cent aqueous solution of hydrogen dioxide. Considerable heat was evolved, and on cooling the oxidation product separated out. This was crystallised from alcohol, and dried in a vacuum over concentrated sulphuric acid.

0·2140 gave 0·5322 CO_2 and 0·0958 H_2O. C = 67·8; H = 4·93.
0·3252 gave 17·2 cc. N_2 at 17° and 746 mm. N = 6·02.
0·3042 gave 0·3118 $BaSO_4$. S = 14·07.
0·1544 in 15·4 naphthalene gave $\Delta t = -0·325°$. M.W. = 216.
$C_{13}H_{11}ONS$ requires C = 68·1; H = 4·80; N = 6·11; S = 13·97 per cent. M.W. = 229.

Thiobenzanilide oxide forms pale yellow microscopic needles, which, when rapidly heated, melt at 162—163°, but decompose at a considerably lower temperature on prolonged heating. It is readily soluble in hot alcohol or benzene, or in warm aniline or nitrobenzene, but is insoluble in water or ether.

116. "*Purification of Acetic Acid.*" By Kennedy Joseph Previté Orton, Muriel Gwendolen Edwards, and Harold King.

Chlorine and bromine do not react with pure acetic acid when light is excluded. Fall in the titre of a solution of bromine in acetic acid, especially if diluted, shows the presence of certain impurities, which are found in the majority of commercial acetic acids. Both fractional distillation and fractional freezing give but small proportions of pure acetic acid.

Distillation from phosphoric oxide, on the other hand, yields 85—90° per cent of the acid free from these impurities. With the proper precautions only traces, 0·009 to 0·04 per cent, of acetic anhydride are produced in this treatment.

117. "*The Detection and Estimation of small Quantities of Acetic Anhydride in Acetic Acid.*" By Muriel Gwendolen Edwards and Kennedy Joseph Previté Orton.

A method of detecting and estimating small quantities of acetic anhydride in aqueous acetic acids was described. The method is based on the fact that certain anilines, notably 2 : 4-dichloroaniline, react with acetic anhydride with great rapidity. The anilide can be separated accurately from the aniline, and then indirectly estimated in the form of chloroamine.

118. "*Tetramethylammonium Hyponitrite and its Decomposition by Heat.*" By Prafulla Chandra Ray and Hemendra Kumar Sen.

A solution of tetramethylammonium hyponitrite when evaporated in a vacuum over sulphuric acid undergoes partial hydrolysis, resulting in the formation of a basic hyponitrite of the quaternary base.

Nitrous oxide, trimethylamine, nitrogen, and methyl ether are the gaseous products of decomposition of tetramethylammonium hyponitrite; a small fraction of the hyponitrite is also converted into nitrate.

119. "*The Second and Third Dissociation Constants of Orthophosphoric Acid.*" By Edmund Brydges Rudhall Prideaux.

A complete account of the changes in hydrogen ion concentration during the neutralisation of the second and third hydrogen ions of orthophosphoric acid has been prepared, partly from the measurements of Salm (*Zeit. Phys. Chem.*, 1907, lvii., 492), and partly from new results. The former results were checked by preparing the solutions in a different way. Equations have been deduced connecting the hydrogen ion concentration of salts of weak polybasic acids with the dissociation constants of these acids.

The second and third dissociation constants of orthophosphoric acid as found by Abbott and Bray (*Journ. Am. Chem. Soc.*, 1909, xxxi., 730) have been tested by means of these results and equations.

The value $k_2 = 2·0 \times 10^{-7}$ has been confirmed, but instead of $k_3 = 3·6 \times 10^{-13}$, $k_3 = 3·0 \times 10^{-12}$ should be substituted as a result of the present work. The revised constants have been used to construct a general equation which it is hoped will be useful to all who require the standards in question.

120. "*Experiments on Tautomerism.* Part I. *The Tautomerism of the System* X·CHR·CR:CR·X, *showing the Identity of the α- and γ-Positions in the Glutaconic Acid Molecule.*" By Ferdinand Bernard Thole and Jocelyn Field Thorpe.

The elimination of a carbethoxy-group as ethyl carbonate in several instances already published has led to the general conclusion that when the terminal hydrogen atoms in systems of the above type are all replaced the tendency for the compound to acquire the hydrogen atom necessary to enable it to react in its tautomeric form is such that any group capable of replacement by hydrogen is at once eliminated in the presence of a suitable reagent. Numerous experiments in support of this view were described.

It was also shown that α-methylglutaconic acid, $CO_2H·CHMe·CH:CH·CO_2H$, and γ-methylglutaconic acid, $CO_2H·CH_2·CH:CMe·CO_2H$, are identical, as are also α-methyl-γ-ethylglutaconic acid,

$$CO_2H·CHMe·CH:CEt·CO_2H,$$

and γ-methyl-α-ethylglutaconic acid,

$$CO_2H·CHEt·CH:CMe·CO_2H.$$

It was suggested that the cause of the identity of the α- and γ-positions in the molecule of glutaconic acid is of the same order as that determining the equality of the meta-positions in the benzene ring.

121. "*Nitrites of the Alkylammonium Bases: Ethylammonium Nitrite, Dimethylammonium Nitrite, and Trimethylammonium Nitrite.*" By Prafulla Chandra Ray and Jitendra Nath Rakshit.

These nitrites are prepared by the interaction of silver nitrite and the corresponding amine hydrochloride. Ethylammonium nitrite, when heated, decomposes according to the equation $2NEtH_3·NO_2 = N_2 + 3H_2O + NEt_2·NO$.

Dimethylammonium nitrite is mainly converted into nitrosodimethylamine, and the decomposition of trimethylammonium nitrite is represented by the equation $3NMe_3H·NO_2 = NMe_3H·NO_3 + 2NO + 2NMe_3 + H_2O$.

122. "*The Relation of Position Isomerism to Optical Activity.* Part IX. *The Rotation of the Menthyl Esters of the Isomeric Fluro- and Iodo-benzoic Acids and of the Halogen Derivatives of the Fatty Acids.*" By Julius Berend Cohen.

In a former paper the apparently anomalous optical relation of the ortho-, meta-, and para-iodobenzoic esters was referred to, and in view of the important effect of temperature, to which attention was drawn, it was decided to re-investigate the rotation of these three compounds (previously determined at 20°) at higher temperatures. This has now been done, and the temperature-rotation curves have been plotted at 20° intervals up to 100°. At 20° the rotations of the three isomerides are identical, $[\alpha]_D$ −61·5°, whilst at 100° there is a slight diminution in the case of the orthoisomeride, $[\alpha]_D$ 61·2°, which is greater in the case of the meta, $[\alpha]_D$ −60·4°, and greatest in that of the para, $[\alpha]_D$ −58°.

The three menthyl fluorobenzoates show among themselves a similar relation to that observed among the chlorine and bromine derivatives, the molecular rotations at 20° of the halogen derivatives being as follows:—

Menthyl ester.	F.	Cl.	Br.	I.
Ortho ..	−194·5	−195	−205	−237
Meta ..	236	237	239	237
Para ..	239	237	239	237

In order to determine the effect of the halogens on optical activity in the aliphatic series, a large number of halogen fatty esters have been prepared; but apart from the fact that the effect on rotation generally increases with the increasing mass or number of the halogen atoms, no satisfactory generalisation was arrived at.

123. "*The Constitution of Dehydro-β-naphthol Sulphide and the Interaction of Sulphuric Acid and Aromatic o-Hydroxysulphoxides.*" By THOMAS PERCY HILDITCH and SAMUEL SMILES.

The investigation of the action of sulphuric acid on the sulphoxides of *p*-cresol and *p*-chlorophenol has been continued. It is found that the primary products are isomeric with the original sulphoxides, but contain the cyclic thioxin system. The formation of these substances is explained by assuming the production of a sulphonium-quinone from the *o*-hydroxy-sulphoxide in the same way that the sulphonium-quinones are formed from the *o*-sulphoxides of diphenylmethane and diphenylamine by the action of acids. This hypothesis is further confirmed by the behaviour of dehydro-β-naphthol sulphide, which has been formerly obtained by alkaline oxidation of β-naphthol sulphide. It was shown that this substance has the sulphonium-quinone structure, $O:C_{10}H_6:S:C_{10}H_6:O$, and that it very readily yields naphthathioxin when treated with alcoholic alkali hydroxide.

124. "*The Action of Steam on Iron at High Temperatures.*" By JOHN ALBERT NEWTON FRIEND, THOMAS ERNEST HULL, and JOSEPH HALLAM BROWN.

The authors have studied the action of steam on iron at various temperatures up to and including 950°. At 500° the reaction was found to be too slow to admit of being carried to completion. The most favourable temperatures for study were found to lie between 650° and 820°. After five hours' heating at 820°, pieces of iron, 0·05 mm. in thickness, were completely converted into ferroso-ferric oxide. At lower temperatures equilibrium appeared to be obtained between the steam and mixtures of ferrous and ferroso-ferric oxide in varying proportions. The explanation that naturally suggests itself is that the outer layers of the metal have been converted into ferroso-ferric oxide, and the rate of diffusion is so slow at the temperatures under consideration that a practically infinite time is required for the oxidation of the interior portions. It was pointed out, however, that this is not the only explanation. It may be that definite mixtures of ferrous oxide and ferroso-ferric oxide are produced, having a lower dissociation pressure than ferroso-ferric oxide, but higher than ferrous oxide, the mixtures being an equilibrium with the steam at the various temperatures corresponding therewith.

(To be continued).

Association of Teachers in Technical Institutions.—The fifth Annual Conference of the Association of Teachers in Technical Institutions will be held this year at Southport on June 5th and 6th. The programme is a long and interesting one, and includes a Presidential Address by the President for this year, Barker North, Esq., of the Bradford Technical College. Among the questions set down for discussion are "The Organisation of Higher Technical Instruction"; "The Representation of Teachers on Educational Bodies"; "The National Organisation of Technical Education"; and "The Salaries and Pensions of Technical Teachers." Full particulars of the Conference can be obtained from the Hon. Secretary of the Association, Mr. P. Abbott, at the Polytechnic, Regent Street.

NOTICES OF BOOKS.

Clarification of Sewage. By Dr. Ing. RUDOLF SCHMEITZNER. Translated by A. ELLIOTT KIMBERLY. New York: The Engineering News Publishing Co. London: Constable and Co., Ltd. 1910. (6s. net).

THIS book contains an excellent account and critical survey of the plant for the clarification of sewage in the larger German cities, which the author studied thoroughly, and although some of the conclusions reached are not in perfect agreement with the results of English practice (for instance, in regard to the disadvantages attendant on the use of septic tanks), the translation is well worth the careful study of sanitary engineers and city officials. The book is concerned solely with the engineering aspect of the subject, the chemistry and bacteriology of sewage clarification being mentioned only incidentally, and the discussions are always well-balanced and critical and exceedingly concise. Tabular statements of the advantages and disadvantages of rival processes and of the factors to be considered in order that the maximum of success may be attained, are frequently given, and the clearness of the whole treatment is a striking characteristic which is altogether beyond praise.

An Introduction to Chemical Theory. By ALEXANDER SCOTT, D.Sc. (Edin.), Sc.D. (Camb.), F.R.S. Second Edition. London: Adam and Charles Black. 1911. (5s. net).

ALTHOUGH ten years have elapsed since this book was first published, comparatively few changes have been made in the second edition, possibly fewer than the importance of recent developments in chemical theory would warrant. Thus the ionic hypothesis is dismissed somewhat summarily, as before, although the years that have passed have brought to light facts which confirm it, and have added to the number of its adherents. On the other hand, the book is one that can be recommended as thoroughly interesting. The historical development of our knowledge of chemical theory is presented in such a way as to awaken and stimulate the student's scientific imagination, and the philosophical treatment is certain to appeal to the more thoughtful readers, while the style is comparatively easy. The theoretical chemistry of the carbon compounds is included in a chapter which gives a good introduction to the study of organic chemistry.

Analytical Reagents, Standards, and Tests. Compiled by EDMUND WHITE, B.Sc. (Lond.), F.I.C. London: Hopkin and Williams, Ltd. 1911. (1s. net).

THIS book contains descriptions of tests for the chemical purity of many common reagents which are in constant use in the analytical laboratory. A complete method of analysing each reagent is not included, only probable impurities or adulterations being considered, but substances answering satisfactorily to the tests described in the text might safely be regarded as quite pure enough not to introduce appreciable errors if used even in the more refined analytical processes. Some notes are added on the properties of trade varieties of the reagents and the most probable impurities present in them.

A Text-book of Gas Manufacture for Students. By JOHN HORNBY. Sixth Edition. London: G. Bell and Sons, Ltd. 1911. (7s. 6d. net).

THE sixth edition of this useful manual on gas manufacture has been brought thoroughly up to date, and it can confidently be recommended as an introduction to the subject specially suitable for the use of students in technical

institutes. The requirements of candidates for the examination of the City and Guilds of London Institute in Gas Manufacture have been kept in view in writing the book, and recent papers set in both the ordinary and honours grade are included. The treatment of the subject is well balanced, and a judicious selection of material has been made, so that only subjects of great importance are discussed in anything approaching detail, and thus room is made for an admirable comprehensive review of the main features of modern methods of gas manufacture. The illustrations are large and clear, and include, as a rule, only such as are of real value to the student, useless pictures of machinery and apparatus being infrequent.

An Introduction to Bacteriological and Enzyme Chemistry. By Gilbert J. Fowler, D.Sc., F.I.C. London: Edward Arnold. (7s. 6d. net).

There was undoubtedly room for this book, and the author is to be congratulated upon having produced a work which will be of the utmost assistance to students as well as to officials whose work requires a knowledge of recent developments of bacteriological chemistry. The growth of the subject has been extraordinarily rapid, and the mass of detail which has been accumulated is somewhat bewildering even to specialists, owing to its apparent lack of cohesion, so that a book dealing only with main principles will be very welcome on all sides. The elements of bacteriology are excellently treated, but the outlines of organic chemistry, which must be understood in order that real progress can be made, are more difficult to deal with, and it seems rather doubtful whether the probable requirements of the student who has not already had a thorough grounding in organic chemistry are satisfactorily met. The author, who has had the advantage of the assistance of other experts in writing some portions of the book, is particularly happy in his treatment of applied bacteriology; *e.g.*, the bacteriological chemistry of dairy products and of sewage purification.

Matriculation Directory, January, 1911. London: University Tutorial Press, Ltd. (1s. net).

The Matriculation Directory for January, 1911, contains the usual features, namely, hints on courses of work and the choice of text-books, the papers set in the January examination, and solutions of some of them together with some criticisms of the questions, from which intending candidates can gather whether they were more or less difficult than usual. The book will undoubtedly be most useful to candidates for the examination, and teachers also who are preparing students for it will be able to glean some hints from the discussions of the relative difficulty of the different subjects.

Grundriss der Kolloidchemie. ("Outlines of Colloidal Chemistry"). By Dr. W. Ostwald. Second Edition. Part I. Dresden: Theodor Steinkopff. 1911. (9 marks).

Many additions and alterations have been made in the text of this authoritative work on colloidal chemistry, which comes from the pen of a chemist who has perhaps done more than any man living to increase our knowledge of the subject, and to establish it upon a firm experimental basis. The book is to be issued in two parts, of which this is the first, and contains chapters on general colloidal chemistry in which the theory of the colloidal state is fully and clearly discussed, and also includes the special part dealing with the physico-chemical and mechanical properties of colloids, leaving electrical and optical properties, &c., for the second volume. It is no doubt unnecessary to emphasise the fact that the treatment is clear, comprehensive, and systematic; the author's unique knowledge of his subject enables him to generalise and summarise in the most effective and convincing manner, and the references to periodical and other literature are complete and bring the subject down to the most recent possible date.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 11, March 13, 1911.

Alterability of Aluminium.—H. Le Chatelier.—On photographing specimens of altered and unaltered aluminium after attacking them with sodium chloride for one minute under the action of an electric current, it is seen that in the unaltered specimens there are black holes irregularly scattered over the surface, while the altered specimens exhibit a continuous cellular network similar to that of most metals when crystallised by fusion. Previous to the action of the sodium chloride this network was visible only in the neighbourhood of the surface in the regions which are most altered. The disintegration of the metal evidently results from the opening of the cellular joints owing to either a mechanical or chemical action.

Catalytic Condensation of Ether Salts by Metallic Oxides.—Paul Sabatier and A. Mailhe.—When an ether salt formed from a primary formic alcohol and a monobasic organic acid is heated in presence of a catalysing oxide, MO, the following reaction occurs:—

$$2(RCOOC_nH_{2n+1}) + 2MO = (RCOO)_2M + (C_nH_{2n+1}O)_2M.$$

Both the salt, $(RCOO)_2M$, and the alcoholic derivative, $(C_nH_{2n+1}O)_2M$, are unstable if the oxide used is a catalyser for both the acid and the alcohol employed. If they are equally unstable they decompose simultaneously:—

$$2(RCOOC_nH_{2n+1}) + 2MO = \begin{cases} \text{ketone} & RCOR + CO_2 + MO \\ \text{hydrocarbon} & 2C_nH_{2n} + H_2O + MO \end{cases}$$

If the catalyser has more action on the acid than on the alcohol the alcohol is regenerated—

$$(C_nH_{2n+1}O)2M + H_2O = MO + 2C_nH_{2n+1}OH,$$

and the whole reaction is—

$$4(RCOOC_nH_{2n+1})_2 = = 2RCOR + 2CO_2 + 2C_nH_{2n} + 2(C_nH_{2n+1}OH).$$

On the other hand, if the catalyser has less action on the acid the free acid is formed,—

$$(RCOO)_2M + H_2O = MO + 2(RCOOH).$$

Oxides which are incapable of acting on the acids give the following reactions:—

$$2(RCOOC_nH_{2n+1}) + MO = M(OC_nH_{2n+1})_2 + (RCO)_2O = MO + 2C_nH_{2n} + H_2O + (RCO)_2O = MO + 2C_nH_{2n} + 2(RCOOH).$$

Magnetism of Complex Salts.—E. Feytis. Using a Curie's balance the author has determined the magnetic molecular susceptibility of various complex salts of iron, cobalt, platinum, &c., and has thus confirmed the results of Wiedemann and Pascal.

Determination of Molecular Weight of Uranous Oxide.—W. Œchsner de Coninck.—To determine the molecular weight of uranous oxide, the author subjected uranyl chloride to the action of hydrogen at a dark red heat, $UO_2Cl_2 + H_2 = 2HCl + UO_2$. The mean value found for the molecular weight in five determinations was 270·07.

Oxidation of Iodine by Hydrogen Peroxide.—V. Auger.—When a hydriodic acid solution of iodine is treated with hydrochloric acid and hydrogen peroxide, iodic acid is formed by a series of reactions, which are represented by the following equations:—

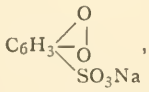
$$2HCl + H_2O_2 = 2H_2O + Cl_2$$
$$I + 3Cl = ICl_3$$
$$5ICl_3 + 9H_2O \rightleftarrows 3IO_3H + 15HCl + I_2.$$

Some well-defined Bismuthides.—A. G. Vournasos.—In boiling paraffin potassium and sodium combine with bismuth, giving definite products, Na_3Bi and K_3Bi, independently of the proportions in which the constituents are present. Na_3Bi forms little crystalline lamellæ of a blackish grey colour. Both bismuthides are easily oxidised in the air, and give a black powder consisting of suboxide of bismuth and alkali. The products readily catch fire, leaving a residue formed of a brick-red alkaline bismuthate. The bismuthides slowly decompose water at the ordinary temperature, yielding caustic alkali and a black powder consisting of bismuth oxide and bismuth. They reduce soluble cupric salts, giving a characteristic precipitate of copper. They absorb hydrogen at 350°, probably with formation of solid BiH_3.

Exact Method of Determining Ash in Animal and Vegetable Products.—E. Fleurent and Lucien Lévi.—In determining ash by calcination there is a loss of phosphorus, the amount of which varies between very wide limits. The causes of this loss are three in number:—(1) The action of carbon; (2) the action of silica on the acid phosphates in the ash; (3) The conversion of the phosphorus into a volatile compound by the fatty matter in the substance. To obviate this loss the authors recommend the following procedure:—(1) The removal of fat in materials which are rich in it; (2) the carbonisation of the substance in a platinum crucible at as low a temperature as possible; (3) treatment of the powdered residue with milk of lime; (4) Evaporation to dryness and calcination by Schlœsing's method. In the final weighing the amount of lime added must be taken into account.

Vol. clii., No. 12, March 20, 1911.

Differentiation of the Latent Images obtained with Emulsions of Silver Chloride and Bromide.—L. Lumière and A. Seyewetz.—Quinone sulphonate of sodium,—



is a substance which develops the latent impression of emulsions of silver gelatino-chloride without acting appreciably on those of the gelatino-bromide. The substance itself has no reducing properties, and is, in fact, an energetic oxidising agent, but it acts as a reducer when a solution of sodium sulphite is added to it. The following mixture may be used:—Water, 1000 cc.; quinone sulphonate of sodium, 10 grms.; anhydrous sodium sulphite, 50 grms. Pyrogallic acid behaves similarly.

MISCELLANEOUS.

Chemical Society.—Faraday Lecture.—An Extra Meeting of the Chemical Society will be held, by the kind permission of the Managers, in the Theatre of the Royal Institution, 21, Albemarle Street, W., on Wednesday, June 14th, 1911, at 8 p.m., when the Faraday Lecture, entitled "The Fundamental Properties of the Elements," will be delivered by Prof. Theodore W. Richards. Admission will be by ticket only. Each Fellow of the Society is entitled to two tickets, application for which should be made as early as possible to the Assistant Secretary, Chemical Society, Burlington House, Piccadilly, W.

Royal Institution.—On Tuesday next, May 30, at 3 o'clock, Prof. W. W. Watts delivers the first of two lectures at the Royal Institution on "Charnwood Forest—its Ancient Volcano and its Fossil Landscape." On Thursday, June 1, Mr. T. Thorne Baker commences a course of two lectures on (1) "Changes Effected by Light," (2) "Practical Progress in Wireless Telegraphy"; and on Saturday, June 3, Dr. W. L. Courtney begins a course of two lectures on "Types of Greek Women." The Friday Evening Discourse on June 2 will be delivered by Commendatore G. Marconi on "Radiotelegraphy," and on June 9 by Prof. Svante Arrhenius on "Applications of Physical Chemistry to the Doctrine of Immunity."

University of London.—A course of five lectures on "The Application of Hyperbolic Functions to Electrical Engineering Problems" will be given at the Institution of Electrical Engineers, Victoria Embankment, by Dr. A. E. Kennelly, at 5.30 p.m., on May 29th, 30th, 31st, and June 1st and 2nd, 1911.

Syllabus.

May 29. Hyperbolic Angles and their Properties; The Relations between Circular and Hyperbolic Angles; Applications of Hyperbolic Functions to Continuous-current lines of Uniform Resistance and Leakance.

May 30. The Simple Representation of Artificial Lines, and Alternating-current Lines by Hyperbolic Angles; Equivalent Lines (T and π).

May 31. The Distribution of Voltage and Current over Alternating-current Power-transmission Lines as Simplified by the use of Hyperbolic Angles.

June 1. The Distribution of Voltage and Current over Telephone Lines, both Simple and Loaded—(1) by Hyperbolic Angles; (2) by Equivalent Circuits.

June 2—The Hyperbolic Theory of Voltage and Current on Composite Telephone Lines and on Long Submarine Telegraph Cables. Miscellaneous Applications of Hyperbolic Functions in Electrical Engineering.

The lectures are addressed to advanced students of the University and others interested in the subject dealt with. Admission will be by ticket obtainable on application to the Secretary of the Institution of Electrical Engineers, Victoria Embankment, W.C.

MEETINGS FOR THE WEEK.

TUESDAY, 30th.—Royal Institution, 3. "The Ancient Volcano of Charnwood Forest, Leicestershire," by W. W. Watts, F.R.S.

WEDNESDAY, 31st. Society of Public Analysts, 8. "Composition of Milk," by H. D. Richmond. "Analysis of Margarine," by C. H. Cribb and P. A. E. Richards. "Some Methods of Estimating Cocoanut Oil and Butter in Butter and Margarine" and "Further Analyses of Ghee," by C. Revis and E. R. Bolton. "Estimation of Quinine as the Acid Citrate in certain Organic Liquids," by T. Cockburn and J. W. Black. "Determination of the Amount of Dissolved Oxygen Absorbed by Sewage Effluents containing Nitrite, and of the Amount of Nitrite in Sewage Effluents or Water," by R. W. Clarke.

THURSDAY, June 1st.—Royal Institution, 3. "Changes effected by Light," by T. Thorne Baker, F.C.S.

—— Royal Society. "Experiments on the Restoration of Paralysed Muscles by means of Nerve Anastomosis," by R. Kennedy. "Mechanism of Carbon Assimilation," by F. L. Usher and J. H. Priestley. "Action of Radium Radiations upon some of the Main Constituents of Normal Blood," by Miss Helen Chambers and S. Russ. "The Pathogenic Agent in a Case of Human Trypanosomiasis in Nyasaland," by H. S. Stannus and W. Yorke. "Experimental Transmission of Goitre from Man to Animals," by Capt. R. McCarrison.

—— Chemical, 8.30. "Dissociation Pressures of the Alkali Bicarbonates—Part I., Sodium Bicarbonate," by R. M. Caven and H. J. S. Sand. "Absorption Spectra of Cinchonine, Quinine, and their Isomers," by J. J. Dobbie and A. Lauder. "Influence of Conjugated Linkings upon General Absorptive Power—Part II., Some Open-chain and Cyclic Compounds," by C. R. Crymble, A. W. Stewart, R. Wright, and Miss F. W. Rea. "Constituents of the Bulb of *Buphane disticha*," by F. Tutin. "New Derivatives of Aminolauronic Acid," by J. Weir. "The Triazo-Group—Part XVIII., β-Triazoethylamine," by M. O. Forster and S. H. Newman. "The Interaction of Formic Acid and Cellulose," by C. F. Cross and E. J. Bevan. "Configuration of the Stereoisomeric Dibromosuccinic Acids," by A. McKenzie.

FRIDAY, 2nd.—Royal Institution, 9. "Radiotelegraphy," by Commendatore G. Marconi, LL.D., &c.

SATURDAY, 3rd.—Royal Institution, 3. "Types of Greek Women," by W. L. Courtney, M.A.

THE CHEMICAL NEWS.

Vol. CIII., No. 2688.

BANQUET IN HONOUR OF PROFESSOR H. E. ARMSTRONG, F.R.S.

A banquet was given on May 13th to Prof. H. E. Armstrong, Ph.D., LL.D., F.R.S., by his old pupils and friends. The gathering was one of the most representative in all branches of physical and chemical science in which it has been our good fortune to take part, and it speaks volumes to the life-long popularity of Prof. Armstrong that no less than 250 friends gathered round him to testify their esteem and affection; whilst the Imperial importance of the teaching work he has been carrying on for more than forty years is shown by the large number of men eminent in all branches of scientific industry who made up the bulk of those present.

The Banquet took place at the Hotel Cecil, under the Chairmanship of Prof. W. J. Pope, Mr. Maurice Solomon being Vice-Chairman.

The following is an alphabetical list of those who took part in the Banquet:—A. S. E. Ackermann, B.Sc., A.M.I.C.E.; R. Adkin; R. A. Adkin; R. A. Appleyard; J. S. Arkinstall; E. F. Armstrong, Ph.D., D.Sc., F.C.G.I.; H. C. Armstrong; H. L. Armstrong; Dr. R. R. Armstrong; P. S. Arup, M.A., B.Sc.; H. B. Baker, M.A., D.Sc., F.R.S.; J. L. Baker, F.I.C.; G. Barger, M.A., D.Sc.; W. Barlow, F.R.S.; W. Phipson Beale, K.C., M.P.; S. Becton; G. T. Beilby, LL.D., F.R.S.; W. G. Bennett, B.Sc.; R. Berncastle; W. G. Black, F.I.C.; R. Blair, M.A.; M. B. Blackler, Ph.D.; P. Blenkinsop; R. Blenkinsop; H. C. Booth, M.I.C.E., F.C.G.I.; H. Borns, Ph.D.; Dr. E. C. Bousfield, D.P.H.; E. G. P. Bousfield; A. H. Brind; Prof. A. J. Brown, M.Sc., F.R.S.; G. E. Brown, F.I.C.; H. T. Brown, LL.D., F.R.S.; C. E. Browne, B.Sc.; M. A. Bulloch; R. J. Caldwell, D.Sc.; G. G. Carter; A. C. Chapman, F.I.C.; D. L. Chapman, M.A.; B. Chatterton, A.M.I.C.E.; J. Chegwyn, M.A.; J. H. Clarke; F. Clowes, D.Sc.; R. T. Colgate; H. G. Colman, D.Sc., Ph.D.; W. R. Cooper, M.A., B.Sc., M.I.E.E.; J. H. Cowham, LL.D.; Prof. H. Crompton; Sir Wm. Crookes, O.M., D.Sc., LL.D., F.R.S.; C. F. Cross, B.Sc., F.I.C.; Prof. A. W. Crossley, D.Sc., Ph.D., F.R.S.; D. Crothers; A. J. Daish; Prof. W. E. Dalby, M.A., B.Sc., M.I.C.E., M.I.M.E.; W. A. Davis, B.Sc.; C. H. Desch, D.Sc., Ph.D.; Prof. Sir James Dewar, M.A., LL.D., D.Sc., F.R.S.; A. P. Dicksee; Prof. E. Divers, M.D., D.Sc., F.R.S.; J. M. L. Donald; G. C. Donington, M.A.; G. B. Donne; W. P. Dreaper, F.I.C.; C. V. Drysdale, D.Sc., M.I.E.E.; W. Duddell, F.R.S., M.I.E.E., P. Dvorkovitz, F.R.C.S., M.R.N. (Russ.); B. Dyer, D.Sc.; A. Edwards, A.I.C.A.; K. B. Edwards; B. Ellis; J. V. Eyre, Ph.D.; F. M. Farrar; A. Findlay, M.A., D.Sc., Ph.D; M. O. Forster, D.Sc., Ph.D., F.R.S.; J. Franklin; W. H. Franklin; R. C. Gale; J. A. Gardner, M.A.; Prof. M. A. Gerothwohl, Litt.D.; W. S. Gilles, F.I.C.; E. N. Glanville, A.M.I.C.E.; W. H. Glover, Ph.D.; H. Gordon, M.A.; W. Gore, M.I.C.E.; H. W. Gosney; A. J. Greenaway, F.I.C.; Prof. R. A. Gregory; C. J. Guttmann, B.Sc., A.M.I.C.E.; A. D. Hall, M.A., F.R.S.; H. Harding, B.Sc.; J. A. Harker, D.Sc., F.R.S.; E. J. Harper, A.M.I.C.E.; R. S. Haskew; H. C. Haycraft, B.Sc.; L. M. Hawkins, M.A.; E. E. Heller; W. M. Heller, B.Sc.; Prof. G. G. Henderson, M.A., D.Sc.; T. A. Henry, D.Sc.; Prof. J. T. Hewitt, D.Sc., Ph.D., F.R.S.; C. F. Hitchins; J. L. Holland, B.A.; E. F. Hooper; E. G. Hooper, F.I.C.; F. G. Hopkins, M.A., D.Sc., F.R.S.; E. Horton, B.Sc.; W. Houlding, B.Sc.; H. A. Humphrey, F.C.G.I., M.I.C.E., M.I.M.E., M.I.E.E.; A. V. Hussey; H. B. Hutchinson, Ph.D.; P. C. C. Isherwood, Ph.D.; E. C. Jee, D.Sc.; S. H. Jennings, M.A.; W. T. John, B.Sc.; J. E. Johnson, F.I.C.; G. C. Jones, F.I.C.; J. Jones; H. A. D. Jowett, D.Sc.; C. A. Keane, D.Sc., Ph.D., F.I.C.; L. Kemp; W. J. Kemp, F.I.C.; Prof. F. S. Kipping, D.Sc., F.R.S.; C. A. Klein; W. de Lacy-Bacon; C. G. Lamb, M.A., A.M.I.C.E.; G. D. Lander, D.Sc.; A. Lapworth, D.Sc., F.R.S.; C. L. Lavers-Smith; Sir Chas. Lawes-Wittenronge; H. J. de Q. Lenfertey; W. J. Leonard; R. Lessing, Ph.D.; H. R. Le Sueur, D.Sc.; W. A. Lethbridge, B.A.; E. W. Lewis, B.Sc.; A. Liebmann, Ph.D.; F. E. S. Lindley; A. R. Ling, F.I.C.; T. M. Lowry, D.Sc.; G. R. Lynch; A. McKenzie, D.Sc., Ph.D.; Prof. E. W. Marchant, D.Sc.; E. H. Martin; Prof. T. Mather, F.R.S.; G. D. Mathews; E. F. Matthews, B.Sc.; F. E. Matthews, Ph.D.; C. R. Merton, B.Sc.; R. Messel, Ph.D.; S. Miall, LL.D., B.Sc.; Principal H. A. Miers, M.A., D.Sc., F.R.S.; A. K. Miller, Ph.D.; N. H. J. Miller, Ph.D.; H. B. Mole; R. L. Mond, M.A., F.R.S.E.; J. E. Montgomrey, B.Sc., A.M.I.C.E.; G. T. Moody, D.Sc.; G. T. Morgan, D.Sc., A.R.C.Sc.; Hugo Müller, Ph.D., LL.D., D.Sc., F.R.S.; C. S. Mummery; A. H. Mundey, A.I.C.E.; S. S. Napper, F.I.C.; T. G. Nicholson, M.B., B.Sc.; Prof. K. J. P. Orton, M.A., Ph.D.; F. W. Passmore, Ph.D.; J. Percival; Prof. J. Perry, M.E., D.Sc., LL.D., F.R.S.; R. H. Pickard, D.Sc., Ph.D.; Prof. R. H. A. Plimmer, D.Sc.; T. H. Pope, B.Sc.; Prof. W. J. Pope, M.A., M.Sc., F.R.S., F.C.G.I.; J. F. Potts; F. B. Power, Ph.D., LL.D.; A. J. Pugh; F. L. Pyman, D.Sc., Ph.D.; F. C. Raphael, A.M.I.E.E.; J. H. Reeves; F. F. Renwick; C. Revis; H. D. Richmond, F.I.C.; R. Robertson, M.A., D.Sc.; W. Robertson, A.R.C.Sc.; W. H. Robertson; E. H. Rodd; E. C. Rossiter, F.I.C.; A. R. Runeckles, B.Sc.; E. J. Russell, D.Sc.; J. H. Ryffel, M.A., B.Sc.; H. J. S. Sand, Ph.D., D.Sc.; H. C. Sayer; A. A. Schultz; A. W. Schultz, A.I.C.; R. Seligman, Ph.D.; I. Seligman; A. T. Simmons, B.Sc., A.R.C.Sc.; The Rev. Skinner, B.A.; F. E. Smith, A.R.C.Sc.; F. Soddy, M.A., F.R.S.; M. Solomon, M.I.E.E.; A. L. Soper; C. W. Spiers, M.I.E.E.; R. H. H. Stanger, A.M.I.C.E., A.M.I.M.E.; J. E. Stead, F.R.S., D.Met.; C. M. Stuart, M.A.; F. Stuart, B.A.; W. E. Sumpner, D.Sc.; E. Thompson; R. W. Tonkin; J. W. M. Topley, A.M.I.C.E.; G. H. Tripp; G. W. Tripp, A.M.I.C.E., A.M.I.M.E.; T. H. Usherwood, B.Sc.; C. E. Vance; J. Wade, D.Sc.; E. E. Walker; H. Waumsley; H. J. Wheaton; E. Wheeler; Sir Wm. H. White, K.C.B., LL.D., D.Sc., F.R.S., M.I.C.E., M.I.M.E.; R. Whymper; S. Williamson, Ph.D.; J. S. Wilson, A.M.I.C.E.; L. P. Wilson; L. A. H. Winckler; F. P. Worley, M.A., M.Sc.; Prof. W. P. Wynne, D.Sc., F.R.S.; A. C. Young; J. Zeitlin.

After the usual loyal toasts, Prof. Pope, in proposing the health of the guest of the evening, said:—In placing before you the toast of the evening I must first state why this pleasant duty has fallen on me rather than on one of the many present who are my seniors, and who would be better able to do justice to the subject. The movement which culminates to-night was instituted by a number of Professor Armstrong's former students; it was intended as an attempt to express in some coherent form the feelings of gratitude, esteem, and affection in which he is held by all who have passed through his hands as pupils. As soon, however, as it became known that such a function was contemplated, so many of the Professor's old friends and associates expressed such an ardent desire to co-operate, that we felt it would be very ungracious, and, indeed, highly undesirable, to maintain the original restriction. We are thus gathered this evening as a body made up of widely diverse components, to express our appreciation of our guest as a chemist, as a teacher, and as a man.

Whilst we have been able to discard the purely domestic form of our function as at first conceived, and to make it, at short notice, of a far more widely representative character, it has not been possible to effect a complete

metamorphosis. And so this evening's chief toast is being proposed by one of the Professor's former students who has become a chemist, of sorts, and is to be supported by another old student who has achieved distinction as an engineer.

This splendid gathering constitutes a magnificent tribute to our distinguished guest. Its magnitude has proved a source of some embarrassment to the organisers of the the feast; its composition is a source of very real embarrassment to me. Whilst I have been associated with our guest for some two and twenty years, there are some present who have been on terms of unbroken friendship with him for more than twice that period, and who have been able to follow each scientific contribution of his as it appeared at a time when many of us were *in statu nascendi*.

Every chemist present knows much of Dr. Armstrong's scientific work—work which started when the constitution of benzene was hardly understood, before the electrolytic dissociation hypothesis was enunciated, and when the investigation of camphor, the terpenes, and the alkaloids had scarcely begun. The last thirty or forty years has been the Golden Age of chemistry. It has seen the uprearing of the vast fabric of modern organic chemistry, the co-ordination of much of our knowledge of general chemistry, and the building up of many of the great chemical industries. The man who has passed through these times, who has seen each difficult situation in our subject besieged, undermined, and finally carried by storm, who has had the energy and the genius to win for himself a commanding place in the attack: who has, in short, like our guest, written his name on most of the great chemical achievements of the past thirty years—that man has lived, and need envy no one.

But I must pass rapidly from Dr. Armstrong's chemical work—from his contributions to our knowledge of benzene, naphthalene, and camphor, the theory of solutions, the nature of combustion and chemical change, and his recent work on plant physiology and on crystallography—and refer to other phases of his numerous activities. His opportunity as an educationalist came some thirty years years ago when the great City Companies initiated, financed, and established their now famous scheme for the advancement of technical education. How he and his colleagues seized upon and made the most of the opportunity thus afforded them is well known to you all. The many hundreds of my old fellow-students holding honourable appointments all over the globe are the living testimony of the success achieved by the City Livery Companies, through their first appointed Professors to whom we all owe so much.

In the curriculum which was arranged, experimental subjects were taught by practical methods, and each of the important technical sciences was studied in conjunction with the other great subjects auxiliary to it. The course of training, instituted as a perilous experiment so many years ago, has now been adopted as a model by the science schools throughout the country, and its success has become a household word.

It is no part of my task this evening to deal in any exhaustive fashion with the mode of instruction initiated by our guest. It involved an expansion of the ordinary interpretation of a professor's duties towards his pupils. Dr. Armstrong worked in the laboratory side by side with the student: the beneficial effect of the personal contact thus established between the teacher of wide knowledge and mature experience and the junior cannot be overrated. But if the student was careless, lazy, or stupid—and all these faults were too often mine—the personal touch frequently became a heavy one.

During the fifteen years or so which have elapsed since I was loosed from Professor Armstrong's apron-strings, I have taught my subject under a great variety of conditions. Throughout that wide experience the training in fundamentals, which I owe mainly to him, has enabled me always to hold my own.

The wide view which our guest took of his responsibilities towards the student did not lapse when the studen received his diploma. The former chemical students know well that our Professor has always been their best friend, always available as a source of inspiration in connection with scientific work, and always ready with assistance and advice. How much many of them owe to him we shall probably never realise; Dr. Armstrong keeps his good deeds to himself.

The influence which the Professor has exerted upon the development of chemical science by reason of his remarkable breadth of knowledge and experience, his complete disinterestedness, his large school of carefully trained pupils, and the inspiriting effect of his enthusiasm has been enormous. During forty years an unceasing flow of papers has appeared, inspired directly by him, and representing the work of men who have had the privilege of working with him. It is not an exaggeration to say that no living chemist in this country has exercised a more generally stimulating influence on the progress of chemical research than our guest.

We are not met merely to congratulate Dr. Armstrong on his past achievements. We see him amongst us with the same vigour of body and mind, the same enthusiasm, and the same youthfulness of bearing many of us knew so well twenty years ago. We feel that we are expressing no vain hope in wishing him many years of health and strength. We know how those years will be occupied—we rest assured that he will devote the long period of activity before him to the advancement of science and education, and to the promotion of the welfare of his past, his present, and his future students.

Mr. Maurice Solomon:—In rising to second the toast which has been so felicitously proposed, I cannot help feeling that the mantle of Elijah has descended on unworthy shoulders. If the true criterion of Professor Armstrong's teaching is to be found in the proficiency as chemists of those whom he has trained, then there are many in this room far worthier than I to stand in my place at this moment. Fortunately, I have been preceded by Professor Pope, whose chemical attainments are such that there is no possibility of any false impression arising from my own shortcomings in this respect. In one way, however, I think that if I am able to voice, no matter how inadequately, the feelings of engineers who, like myself, have derived immense benefit from Professor Armstrong's teaching, then my selection to second the toast of the evening is not inappropriate.

Professor Armstrong's teaching was something more than the mere teaching of chemistry. It aimed at something more than the training of chemists. It is therefore not unmeet that this toast should be proposed, on the one hand by a distinguished chemist, and on the other by one who can bear testimony to the value of his training apart from its specialisation.

I had occasion a few years ago, in an appreciatory note which I wrote on Professor Ayrton, to express my views on the method of teaching at the college. Much that I wrote then can be said with equal truth of Professor Armstrong, for to a large extent the same spirit inspired both his and his colleague's work.

I fear that I know but little of the methods now in vogue of teaching science in our public schools, but at the time that I was at school, now longer ago than I care to recollect, they could at best be described as, in chemical language, "an unrefined product." An unfortunate impression that the formulæ of chemical compounds were only a substitute for Greek irregular verbs, capable of assimilation by those whose faculty of mental digestion was of an inferior character, had gained an immovable hold on those entrusted with the education of my youth. It is not too much to say that the methods of the college came to me as a revelation, and in no case was the revelation more powerful and more convincing than in the first year's chemical lectures. It was as much the personality of their exponent as the actual teaching which created

indelible impressions, impressions which twelve years of commercial engineering have not made fainter or more dim.

I may have forgotten the various stages by which the phenomenon of the rusting of iron was elucidated, or by which we were led to the discovery of the composition of chalk; but I have not forgotten the real lesson which those investigations taught and were designed to teach. And primarily that lesson was this—it taught that scientific knowledge was not the knowledge of what others had discovered, but the knowledge of how to discover things oneself. You will recollect, gentlemen, how Tomlinson, in Kipling's poem, is refused admission to either Heaven or Hell, because he has done nothing on earth on his own initiative, how—

> Peter twirled the jangling keys in weariness and wrath.
> "Ye ha' heard, ye ha' read, ye ha' thought," he said,
> "and the tale is yet to run.
> By the worth of the body that once ye had
> give answer what ha' ye done?"

and how the devil cried in similar language,—

> "Ye ha' heard, ye ha' read, ye ha' got, good lack,
> and the tale begins afresh,
> Have ye sinned one sin for the pride of the eye
> or the sinful lusts of the flesh?"

Had Tomlinson been one of Professor Armstrong's students neither Peter nor the devil would have been called upon to reject him. Certainly not the devil, because it was at Heaven's gate that he first asked admission and it would have been granted to him.

It is immaterial in what course one's actual work may run, but the prime necessity for success, whether success be reckoned in pounds, shillings, and pence, or what is of much more importance, in justified satisfaction at what one has accomplished, is ability to think and act upon one's own initiative. No method of teaching could be better calculated to develop those faculties than the methods which Professor Armstrong originated and practised with such brilliance. The man of science or the engineer (and I suppose that most of us fall under one or other of these categories) has continuously to deal with new problems as they arise, and to find by himself some solution of the difficulties that beset his path. Upon our ability to deal successfully with these problems depends not only our individual success but our prosperity as an industrial nation, industrial nation is the only prosperity which we can hope and it is not too much to say that prosperity as an to enjoy. At no time more than the present has England stood in greater need of competent men of science, men who can take their place, whether a high one or a low one, in the great industrial work which brings bread to the table and coal to the hearth of 70 or 80 per cent of our population. No praise is too high and no honour is too great for those who have trained the men to carry out this work. It is a task of colossal magnitude even now. It was a far greater task when Professor Armstrong first put his shoulder to the wheel. Now there is a rule and precedent by which one can be guided, examples which can be followed, errors and failures which can be avoided. Then the right way had to be discovered. It is at all times a great thing to be a great teacher; it is a nobler thing by far to be a pioneer amongst great teachers, as he is whom we honour to-night.

Governments may bring in their social welfare budgets, their legislation for insurance against sickness and unemployment, and pensions for the aged, but they perform no greater service to the country than he who educates the youth of the nation to be useful, efficient, and productive citizens. To devote one's self to teaching is to devote one's self to a life involving, of a necessity, many trials and disappointments, but there is also the possibility of great reward—the reward of knowing that those whom one has trained have thereby been enabled to perform with efficiency and success the duties that have been laid upon their shoulders—the reward of knowing that these men recognise the fountain from which their inspiration has been drawn. There is no student who came under Professor Armstrong's hands, who had in him the rudiments of the faculties needed by a chemist or an engineer, who was not helped to develop those faculties to the best of their limits by Professor Armstrong's teaching. There can be no student so far "to dumb forgetfulness a prey" who has not at one time or other said to himself, "I should not be what I now am but for Professor Armstrong's teaching," and to this may be added the still greater reward of knowing that the methods he initiated have been followed and copied throughout the civilised world, and that generations yet unborn will owe a debt of gratitude to Professor Armstrong. The man who performs a work of this kind does something more than perform with efficiency the ordinary duties of a citizen. He gives a definite and appreciable impulse to the progress of civilisation. What greater service can any man perform, and what greater reward can any man have, than to see the value of his work appreciated by his students, and that the depth of their appreciation grows with their experience? Because of that, we are here to night to bear witness to our gratitude to Professor Armstrong for the value of our training in former years, and to assure him that we shall not forget all we owe to his ability and genius.

In reply to Prof. Pope and Mr. Maurice Solomon, Prof. Armstrong said:—It is well known that women are gifted with great powers of insight. A few nights ago, referring to to-day's proceedings, my wife remarked: "I shall be sorry for you; you will be much upset and not know what to say." No words could express my feelings better. I am so much overcome by what has been said that I should like to express my thanks by silence, go home, and after reflection return among you to convey to you the full sense of my gratitude. I have known your Chairman in many capacities. He has spoken of himself as a chemist of sorts he should have said all sorts; but it is the first occasion on which I have known him to figure as a portrait painter. It is evident that he can paint a flattering picture, and although it is not for me to say what elements of truth there are in it, I cannot avoid feeling, in face of the "magnificent tribute," as he has termed it, this meeting affords me, that I have not been entirely unsuccessful. I am taken by surprise. A short time ago I was asked to place myself at the disposal of a few friends for an evening; when consenting, I had no conception that anything of this kind was intended—I supposed merely that we were to have a simple gathering on the lines of the Chemical Club. Gentlemen, I can assure you that I am most deeply affected by this evidence of your good will and sympathy, which are indeed welcome to me at the present time.

Your Chairman refers to the fact that I began my career when chemistry was in a rudimentary state. There are not many here probably who realise how much has happened in my time. I had the good fortune to come under the influence of the great Hofmann, as I became a student at the College of Chemistry in Oxford Street during the last term in which he taught there. Then Frankland took me in hand, and at the beginning of my second year entrusted me, in 1866, with the task of working out the combustion process of water analysis which was afterwards published in our joint na nes (1868). Instead of wasting my time on routine exercises in analysis, I had the inestimable advantage of undertaking research work very early in my career, and I am sure that my future was thereby determined. I well recollect Frankland telling me one day to read the paper in which Graham described the way in which he had extracted oxygen from an india-rubber balloon by means of a Sprengel pump, in connection with his great work on the separation of gases by means of colloid septa. And Frankland then made me a pump, merely by sealing on a side piece to a long length of narrow-bore lead glass tube, which served throughout the experiments. This was the first systematic use of the Sprengel pump. Think what has been done with it since that time by your renowned guest on my right, my old friend Sir William Crookes, as well as by those who have followed him in studying the electric discharge under re-

duced pressure the discoveries to which it has led are marvellous.

I think that even now we do not sufficiently recognise the service which Frankland rendered to the community by the work I have referred to on water analysis; indirectly, it led to a complete overhauling of our sources of water supply, and was the beginning of a great wave of sanitary reform. On leaving Frankland I went to Germany and worked in the laboratory of the arch heretic Kolbe, from whom perhaps I imbibed some of my awkward tendency to express my opinions.

A year or two after I left him Kolbe brought out his process for the manufacture of salicylic acid, which soon became of great importance as an antiseptic, so much so that its introduction marks the beginning of an era in the use of preservatives. Soon after my return to England, I began to work at St. Bartholomew's Hospital with Mathiessen, where I took charge of the special classes for students preparing for the University of London. Mathiessen died in October, 1869. The pioneer work he did on alkaloids is well known, especially that on narcotine with Carey Foster and Wright. Nearly all that we know of alkaloids has been learnt since then.

At this time I became Professor of Chemistry at the London Institution, which gave me the great advantage of an independent position and a laboratory of my own in which I had the opportunity of gradually training myself to work alone.

When a student at the Royal College of Chemistry I had the privilege of having your distinguished guest Horace Brown as my friend. We both enjoyed the advantage of being under O'Sullivan, who was one of the assistants. Then and in after years I often went to Burton-on-Trent to stay with my friend Brown, and thus came into contact with the great Peter Griess, who, in those days, had already done much of his work on diazo-compounds, but they were not yet made use of as dyes. I have therefore witnessed the wonderful development of the colour industry which followed on the introduction of the azo-dyes. When I was a student at the College of Chemistry, not many artificial colours were known besides Perkin's mauve. It is an interesting fact, showing how we are still connected with the past, that one of your guests to-night, my old friend Mr. Lavers Smith, was a manufacturer of mauve from orchella weed in pre-Perkinian days, and that his business was destroyed by Perkin's discovery.

In those early days I have referred to O'Sullivan did the work on starch which was so valuable to the brewing industry. And I well recollect the issue of Pasteur's "Etudes sur la Bière" and the immediate influence it had on my friend Horace Brown, who was soon led by it to introduce his method of forcing beers which has been of such importance to the industry. The marvellous developments in bacteriology and its applications consequent on Pasteur's work are known to all.

To pass on, in 1875 I was a candidate for a post which was gained by a better man. That man I have since learnt to know well, and I have learnt also to value his work above that of most others. I trust I have been one of his staunchest friends; yet even in the case of a friend revenge is sweet, and I have had my revenge to the full. With his full concurrence and active assistance a man has been appointed his colleague, if not his superior officer, who is my pupil—your Chairman to-night. Gentlemen, I feel that I might well rest content with such a result of my work, even if I could lay claim to nothing else. But your Chairman is the outcome of a system. In 1879 the City and Guilds Institute—in consequence of the outcry in the early seventies that we lacked facilities for Technical Education—appointed Prof. Ayrton and myself to start classes in temporary premises in Finsbury. I found the plans already prepared and contracts almost settled for a separate chemical building. My first act was to obtain leave to report on the plans, and I took exception to them on the ground that to be of use in practice chemists needed to know something of mathematics, something of engineering, and of physics besides chemistry. My contention was accepted, and with the co-operation of Prof. Perry and Mr. (now Sir Philip) Magnus, who subsequently became our colleagues, we developed a comprehensive scheme which was soon afterwards embodied in the Finsbury Technical College. Later on, in 1885, when Ayrton and I went to South Kensington and became associated with Profs. Henrici and Unwin, a course was developed on lines similar to those first introduced at Finsbury. A step was thus taken which was of some consequence, especially as the two Colleges, from the beginning, imposed an entrance examination which made it possible to weed out most of those who were unlikely to profit from the instruction. Our College has grown from having nine or ten students in the first year to some four hundred and fifty last year. Our students have been remarkably successful, and are known all the world over. The City and Guilds have reason, I believe, to be satisfied with the work they have done in the cause of education. Had I had the opportunity I should have been glad to have devoted myself to chemistry, but my chief work has been to teach engineers, and I have consequently been able to compare this class of student with students of chemistry. I am satisfied that the two represent different types of mind. As a rule those who have more or less marked engineering proclivities are also of a constructive habit of mind—they tend to look at things more from the outside, and are more prepared to apply the teachings of experience and to set things going; those who show chemical proclivities have more introspective habits of mind, and are more inclined to consider what is going on before them. The one cannot be trained as the other. Education can do very little to change us—men are mostly what they are made by their forefathers; the unfortunate thing is that, in these days, so much is done by education to obscure faculties by overtraining and by requiring attention to too many things. We need to simplify our teaching and to be satisfied with far less than is now asked for.

I appear to have had notions with regard to teaching in my very early days, to judge from letters which I find I wrote to my father. I began to try experiments as soon as I began teaching, and made my full profession of faith at the Education Conference at the Health Exhibition in 1884, and at the British Association Meeting in 1885 in my address to the Chemical Section. My name has since been associated with the Heuristic movement, and I have done my best to encourage teaching in schools which would favour the development of the spirit of inquiry—feeling that the beginning must be made at school. Although I am not satisfied with the progress that has been made, I feel hopeful that a sound foundation has been laid on which, in the future, those free from the prejudices which affect us will be able to build. We are always hearing that Germany is ahead of us. Germans are said to receive a superior preliminary training at school. I do not believe this is true. They are better drilled in classics and in their own literature, but the mathematical training is inferior to ours, and practical science is scarcely known in the German schools. The fact is the Germans are by nature more obedient than we are, and they are a better disciplined people; they are willing to be led by competent leaders, and they know how to make full use of their experts. Here expert is a term of reproach; and there is a general tendency for everybody to manage somebody else's business. Teachers are now threatened with interference in all sorts of ways. The success of our College, I am sure, is due to the fact that we were trusted with its entire management on the educational side. The Institute has exercised financial control, and all our proceedings have been regularly reported to it—but we have been left alone to do the work. My good friend Mr. Blair told us last September, in a most valuable paper "On the Relation of Science to Industry and Commerce," which he gave to the British Association, that the management of all technical institutions and departments of applied science should be put on a business footing. The chief need, he

said, was that of consultative committees composed of industrial or commercial leaders or experts of the highest reputation. I would suggest to Mr. Blair that he undertake an inquiry similar to that which he made into technical education into the ways of business men and manufacturers; as a result, he will find it desirable, I think, to propose the formation of consultative committees of teachers to advise the business men. When the two kinds of committee come together, if they are composed of sensible men, probably there will be agreement that it is best for each party to look after its own business.

Five Fellowships of the Royal Society and three Professorships have already fallen to men from my own department.

It was said formerly that it was necessary to go to Germany for a chemical training. We have proved that this is no longer the case. Of the three members of my staff who have obtained Professorships, two—your Chairman being one—have no German taint about them.

One other subject I must mention—crystallography. Knowing the inability of chemists to describe the substances they prepare, and feeling my own inability, it appeared to me desirable to include this subject in our regular course of instruction. Thanks to the assistance which I received from Dr. Hugh Müller, then on the Committee of our Institute, as well as to the help given to me by Mr. Story Maskelyne and Mr. Fletcher, of the British Museum, my recommendation was adopted. The foundation laid by our first instructor, Principal Miers, then a member of the staff of the Natural History Museum, was so secure that we have carried on the work with advantage ever since. As proof of success, I again refer to your Chairman—had he not received such instruction, he would scarcely have been able to co-operate with Mr. Barlow in elaborating the remarkable theory correlating crystalline form with chemical structure which we owe to them. It is peculiarly gratifying to me that I, the pupil of the man who invented valency, should have as pupil a man who has advanced the subject more than any one since van 't Hoff gave us the doctrine of tetrahedral carbon by laying what, I fancy, will prove to be the chief corner stone of the edifice.

Whatever has been done, however, I could have done little without the assistance of the many able men who have been members of my staff—such men as Dr. A. K. Miller, Dr. Kipping, and Dr. Wynne, not to mention others. Most of you know what brilliant work Kipping and Wynne have done. I desire also to record my very special thanks to Dr. Moody. Most of you know what an extraordinary influence he exercised in our college—how he has fathered students and impressed on them the value of business aptitudes. Lastly, I cannot omit to recognise the assistance given to me at all times by one who is not a member of our professional staff—Mr. John Jones, our Registrar.

Gentlemen, I can assure you this occasion must always remain in my memory. The encouragement I have received to-night will enable me, I trust, to make good use of whatever time is left to me.

The health of "The Guests" was proposed by Dr. M. O. Forster, F.R.S., and responded to by Mr. W. Phipson Beale, K.C., M.P., and Prof. Sir James Dewar, F.R.S.

Gases Evolved by the Walls of Glass, Porcelain, and Silica Tubes.—Marcel Guichard.—In order to determine most accurately the amount of gas evolved by the walls of tubes, it is best to ascertain the changes of pressure by means of a McLeod manometer. Jena glass gives hardly any gas in the cold. At 600° about 0·03 cc. of gas per 100 cq. cm. is liberated. The amount set free by porcelain tubes varies very much according to the composition of the porcelain. Opaque silica tubes possess visible small canals filled with gas.—*Comptes Rendus*, clii., No. 13.

ORGANIC AMALGAMS: SUBSTANCES WITH METALLIC PROPERTIES COMPOSED IN PART OF NON METALLIC ELEMENTS.*

By HERBERT N. McCOY and WILLIAM C. MOORE.

(Continued from p. 233).

C. *Properties of Tetramethyl Ammonium Amalgam.*

Physical Properties.—As prepared above, at temperatures of from 10° to −5° the amalgam is a pasty *crystalline* mass about the colour of metallic zinc. While at 0° or at temperatures slightly above 0° the crystalline structure is not so pronounced, yet on several occasions almost solid lumps have been observed in the amalgam formed at 0°. It is somewhat lighter than mercury, as it always floats on the latter. There is evidence that more than one active phase exists in the amalgam. The surface tension of the amalgam is less than that of mercury. There is little tendency, from −10° to 0°, toward inflation of the amalgam, but when the temperature of a sample, washed with absolute alcohol and partially dried with filter-paper, was allowed to rise slowly, the volume increased and at 25° was about twice the volume at 0°.

Stability of the Amalgam.—When the temperature of the clean amalgam is kept near 0° it is quite stable, but on allowing the temperature to rise it decomposes very rapidly. Trimethylamine is one of the products of this decomposition, as is shown by the powerful fish-like odour. The other products have not been fully investigated; it is hoped to make a further study of this point.

General Chemical Properties.—If the amalgam is run from the electrolytic cell directly into a clean dry flask it becomes covered with a grey-white crust, probably tetramethyl ammonium hydroxide, as it reacts with water to form an intensely alkaline solution.

The Reaction of Water on the Amalgam.—When allowed to come in contact with water a violent action takes place; hydrogen is formed and the whole of the mixture becomes ink-black, rapidly turning grey, and a grey colloidal solution is the final result. Le Blanc (*loc. cit.*) probably got the same substance by the electrolysis of aqueous solutions of tetramethyl ammonium chloride, using a mercury cathode a result we have also obtained under similar conditions. We studied the phenomenon further as follows:—

The amalgam was formed as usual in the apparatus described above. After the current had been allowed to run for some time the excess of mercury was drawn off into a clean dry dish. The amalgam was then drawn off into a second small porcelain dish, quickly washed several times with absolute alcohol, dried with filter-paper, and the dish held in the hand against the inside edge of a 600 cc. beaker. A fine stream of water was now forcibly directed against the upper surface of the amalgam, near the lip of the dish, in such a way that the colloidal black deposit was swept into the beaker without carrying along globules of mercury. The washing with water was continued until little or no further action between the amalgam and the water was noticed. When the main portion of the "black deposit" had been swept into the beaker, in nearly every case a black, nearly solid residue, small in amount, was noticed floating on the globule of mercury left. This black substance acted less vigorously with water than the pasty amalgam, but still gave a "colloidal black deposit" with water. An explanation of this fact will be taken up later. The above outlined process was repeated a number of times, until sufficient material had been accumulated; the black residue was then filtered off through a weighed Gooch crucible, dried at 108—110°, and weighed; the filtrate was reserved for further experimentation. This weighed residue was then dissolved in hot nitric acid, repeatedly evaporated with concentrated

* Preliminary report read at the Detroit Meeting of the American Chemical Society, June, 1909 (*Science*, 1909, xxx., 315). From the *Journal of the American Chemical Society*, xxxiii., No. 3.

hydrochloric acid until nitric acid was practically completely eliminated, then diluted, filtered free from asbestos fibres, and the mercury precipitated by hydrogen sulphide. This precipitate was washed, dried, washed several times with carbon disulphide, dried at 108—110°, and weighed. In three analyses in which from 0·4 to 0·8 grm. of substance was taken the percentage of mercury found were 98·06, 97·93, 96·98.

These low but consistent values of the mercury content of the black deposit mean that the substance is in all probability the pure element, the low values being due either to (1) water absorbed to a slight degree, or (2) to a little occluded hydrogen. Less plausible would be the assumption that (1) the deposit is a mixture of mercury and mercurous oxide, or (2) that it is a compound containing the tetramethyl ammonium radical. The deposit after drying generally aggregated into actual globules, and the portion which did not do so became silvery white in colour; this disposes of the first assumption, and there is no other evidence in favour of the second. The mercury itself, used in the preparation of the particular amalgams from which the black deposit was obtained for analysis, was, by analysis, 99·86 per cent pure. The nature of the impurity was not determined.

The filtrates from each of the above experiments and a number of others were titrated with standard hydrochloric acid; the results were calculated to $N(CH_3)_4$ and the ratio, $N(CH_3)_4$ to Hg, was determined from these results, and from the weight of the colloidal mercury. In the table below, in the experiments in which the values "calculated weight, $N(CH_3)_4Cl$" and "actual weight, $N(CH_3)_4Cl$" are given, the solutions after titration were actually evaporated to dryness, and the residues weighed. These residues were then combined, purified, and analysed as shown in Table I.

TABLE I.

Expt. No.	0·1 N HCl (cc.)	Weight colloidal Hg (98 per cent).	$N(CH_3)_4$ calc.	A.	Weight residue.	Cal. weight $N(CH_3)_4Cl$.
270	4·00	0·1329	0·0297	1·66	—	—
271	2·50	0·0515	0·0186	1·02	—	—
272	9·50	0·2303	0·0705	1·21	—	—
273	5·82	0·4496	0·0431	3·87	—	—
274	12·72	0·2797	0·0943	1·10		—
277	7·12	0·3037	0·0527	2·13	—	—
279	18·18	0·3629	0·1348	0·99	0·230	0·199
282	11·11	0·7946	0·0823	3·57	—	—
283	15·43	1·3451	0·1143	4·35	0·180	0·169
285	26·17	0·3713	0·1938	0·71	0·294	0·286
288	12·28	0·4161	0·0910	1·69	0·126	0·134
291	35·50	0·4607	0·2630	0·60	0·395	0·389
292	23·71	0·4983	0·1757	1·05	0·252	0·260

In the column headed "A" is given the number of atoms of colloidal mercury formed for each tetramethyl ammonium ion set free. It is seen that this ratio is not constant. Four of the thirteen values, however, are close to *unity*, which may indicate a possible compound of the formula $HgN(CH_3)_4$. Since the colloid analysed to 98 per cent mercury, this per cent of the *actual* weight of the colloid is used in the calculations.

In several of the experiments in which the colloidal mercury was not used for analysis, it was weighed on dried filter-papers. In some cases the deposit was coagulated by the addition of sodium chloride, and in others by the addition of concentrated hydrochloric acid. The latter, however, was abandoned as a coagulant since it dissolved some of the deposit, though not much. In experiments 270, 271, 272, 273 phenolphthalein was the indicator used, while in the rest of the experiments methyl orange was used.

The values in column "A" are to be taken as approximate only, as it was always difficult to remove every trace of the colloid from the small dish to the beaker by means of wash water. Again, there was always a slight decomposition of the amalgam not due to the action of water.

As stated above, the residues of supposed tetramethyl ammonium chloride left on evaporating to dryness the solutions in experiments 279, 283, 285, 288, 291, and 292 were combined and analysed. This analysis was made as follows:—The combined residues were dissolved in water, the solution evaporated to dryness, the resulting mass taken up with absolute alcohol and precipitated with ether. From the mother liquor of this ethereal solution a second crop of crystals was obtained, and this was re-crystallised from absolute ethyl alcohol. These samples were dried, and weighed portions dissolved in water and titrated with decinormal silver nitrate, using potassium chromate as indicator. 0·1290 grm. of salt of first crystallisation required 11·82 cc. of 0·1 N $AgNO_3$; 0·1044 grm. of salt of second crystallisation required 9·55 cc. 0·1 N $AgNO_3$. Per cent Cl calculated for $N(CH_3)_4Cl$, 32·36. Found: I., 32·27; II., 32·47. The results of these two analyses, with the close agreement between the actual and calculated weights of $N(CH_3)_4Cl$, show conclusively that the amalgam contains the tetramethyl ammonium group.

Two analyses of the gas evolved when the amalgam reacts with water were made as follows:—A quantity of the amalgam was run out into a small dish and quickly washed with absolute alcohol and dried as much as possible by means of filter-paper. It was then decomposed by water and the gas evolved collected. This process was repeated until an amount of gas sufficient for analysis was obtained. The gas was then transferred to a eudiometer filled with mercury, measured, mixed with air, measured, exploded, and the contraction noted. Concentrated sodium hydroxide was now admitted to the tube, but no contraction resulted, hence no carbon dioxide was formed on explosion. In the first analysis 11·00 cc. of the unknown gas were used, and the contraction of the mixture on explosion was 15·30 cc., equivalent to 92·73 per cent of hydrogen; while in the second case 6·50 cc. was the contraction when 4·6 cc. of the unknown gas were used, indicating 94·13 per cent of hydrogen present.

These experiments should be regarded as qualitative only; no corrections were made for the vapour pressure of water; the experiments were made simply to demonstrate that hydrogen is the gas evolved when the amalgam is treated with water, and that no gas containing carbon was produced.

Reaction of the Amalgam with Aqueous Solutions of various Salts.—A cold concentrated solution of ammonium chloride was treated with tetramethyl ammonium amalgam. Ammonium amalgam, as shown by the inflation peculiar to this substance, was formed. *There were absolutely no indications of colloidal mercury.* Part of the same tetramethyl ammonium amalgam reacted in the usual way with water. A saturated solution of potassium chloride was treated with tetramethyl ammonium amalgam at room temperature. There was only a trace of colloidal mercury formed. After the mixture had stood for three minutes the residual mercury was washed quickly six or seven times with water, and then allowed to stand in contact with water. There was absolutely no indication of the presence of tetramethyl ammonium amalgam, but there was a slow reaction between the mercury and the water, gas being evolved. That potassium amalgam had been formed was proved by acidifying the aqueous solution with hydrochloric acid, adding a few drops of chloroplatinic acid, and evaporating to dryness; the residue, when treated with water, remained for the most part undissolved; the yellow crystals were undoubtedly potassium chloroplatinate. A solution of sodium chloride, approximately three times normal strength, was treated with tetramethyl ammonium amalgam. No colloidal mercury was formed, but a quiet action ensued between the solution and the amalgam. This was allowed to continue for four minutes, then the mercury was quickly washed twelve times with cold water and covered with water. Gas was evolved for more than two hours. The resulting solution was alkaline to litmus

—conclusive proof that sodium had replaced the tetramethyl ammonium group in the amalgam. Concentrated solutions of cæsium and rubidium chlorides in water and thrice normal potassium chloride were each treated with parts of the same lot of tetramethyl ammonium amalgam. With the cæsium chloride violent action occurred with the formation of colloidal mercury, but the action was less violent than when pure water alone is used. With the rubidium chloride only a little colloidal mercury was formed, and with the potassium chloride none at all. When the experiment was repeated, using normal solutions of each salt in water, the results were in the same order, the only difference being that with potassium chloride a little colloidal mercury was formed, less, however, than with rubidium chloride.

An aqueous solution of copper sulphate of unknown concentration was treated with tetramethyl ammonium amalgam. The action was fairly violent; only a little colloidal mercury was formed. There was effervescence, and after standing fifteen minutes the mercury was covered with bubbles of gas. At this stage, very thin copper-red crystals were noticed floating on the surface of the supernatant liquid. The mercury itself had a coppery colour. It was washed seven or eight times with water, and showed every indication of the presence of copper amalgam. Part of it was dissolved in nitric acid, the resulting solution evaporated, and ammonium hydroxide added to the *greenish* residue. The characteristic blue colour of the cupriammonium ion was seen while some of the original mercury from which the amalgam had been formed gave absolutely no indications of the presence of copper on similar treatment.

Mercuric chloride in aqueous solutions was also treated with tetramethyl ammonium amalgam; the reduction to the mercurous state was more rapid than when pure mercury acts on mercuric chloride. Colloidal mercury was formed. The flocculent grey precipitate was filtered off and tested with ammonium hydroxide; the characteristic black colour which this reagent affords with mercurous chloride was produced.

Normal aqueous hydrochloric acid acts vigorously on tetramethyl ammonium amalgam, only a little colloid, however, being formed. We have also shown (McCoy and Moore, *Science*, xxx., 315, September 3, 1909) that the amalgam precipitates copper and zinc from alcoholic solutions of their nitrates. All these experiments go to show the complete analogy between the tetramethyl ammonium radical and an ordinary alkali metal, and will be referred to again after the consideration of further experimental work.

The Action of Alcohol on the Amalgam.—One of the first properties of the amalgam to be studied was the reaction with alcohol. The speed of this reaction was determined, approximately, at 0° as follows:—The amalgam was made in the usual way; it was washed four times with absolute alcohol and then immediately poured into absolute alcohol in a conductivity cell at 0°. The resistance of the solution was determined at definite intervals, and from the values for this resistance at the various times the speed of the reaction was calculated, applying the formula for a unimolecular reaction, $k = 1/t \log_e a/(a-x)$. The mixture was, of course, stirred to insure uniformity of concentration as far as possible. If W is the resistance at the time t, and W_a is the final resistance, it is easy to show that $k = 1/t \log_e W/(W - W_a)$, since the initial resistance, that of pure alcohol, is very high. Using this formula, k, the rate of formation of the tetramethyl ammonium ion when the amalgam is in contact with absolute ethyl alcohol is calculated from the results given in Table II.

(To be continued).

TABLE II.

Time, t (minutes).	Resistance (ohms) W.	k.
	Experiment No. 33.	
0	61,600	—
11·5	840	0·0238
21·5	308	0·0492
31·5	264	0·0456
41·5	234	0·0472
51·5	205	0·0752
61·5	201	—
71·5	201	—
81·5	201	—
	Experiment No. 35.	
0	15,400	—
3	399	0·1136
6	300	0·0708
9	250	0·0686
12	215	0·0648
16	194	0·0563
19	173	0·0577
24	150	0·0609
29	139	0·0606
34	129	0·0646
40	117	0·0833
83	115	—
100	115	—

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 18th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Properties of Colloidal Systems. II. On Adsorption as Preliminary to Chemical Reaction.*" By Prof. W. M. BAYLISS, F.R.S.

The existence of an "adsorption-compound" containing acid and base uncombined chemically, and which can be isolated, is described, together with the manner of its conversion into the true chemical compound or salt.

It is shown that a similar kind of compound is formed between an enzyme and its substrate, preliminary to the particular chemical change brought about by the enzyme in question.

Adsorption between enzyme and substrate as affected by the presence of neutral salts is investigated and found to follow the laws of "electrical" adsorption.

The relation between the concentration of an enzyme and its activity is shown to be expressed by an exponential formula, the value of the exponent varying considerably according to circumstances. In certain conditions it may be unity and in others the square root, but is usually between the two.

Accordingly, the view that the rate of an enzyme action at any given moment is a function of the amount of the adsorption compound of enzyme and substrate in existence at that time is to be regarded as fairly well established.

"*Inbreeding in a Stable Simple Mendelian Population, with Special Reference to Cousin Marriage.*" By S. M. JACOB, I.C.S.

"*Direct Guaiacum Reaction given by Plant Extracts.*" By Miss M. WHELDALE.

Previous work on oxidising enzymes has led to the interpretation of the direct blueing action in terms of the activity of a system consisting of an organic peroxide in conjunction with a peroxidase.

The author finds that the power to give the direct action possessed by water-extracts of tissues is accompanied by another phenomenon, *i.e.*, the formation of brown or reddish brown pigments in the tissues on exposure to chloroform vapour. Both phenomena are characteristic

of certain Natural Orders, but are absent from others or are characteristic of certain genera only in an Order. When the direct action is not given, the plant extract will blue guaiacum on addition of hydrogen peroxide (indirect action) and the tissues do not show change of colour in chloroform vapour in the same period of time. The phenomenon of direct blueing of guaiacum is considered by the author to be the outcome of the presence of the dihydric phenol-pyrocatechin in the plants examined.

Pyrocatechin is oxidised on the death of the tissues and then acts as a peroxide enabling the peroxidase, which is almost universally present, to transfer oxygen to the guaiacum. These conclusions are based on following evidence:—(1) That pyrocatechin can be detected in plants (such as have been examined) which give the direct action and show change of colour in chloroform, whereas it cannot be detected in plants lacking these characteristics; (2) That solutions of both chemically-prepared pyrocatechin and the actual plant product, after oxidation in air, will give a direct action with guaiacum and peroxidase only. The same result is not obtained with phenols having the hydroxyl groups in other positions. Hence the *direct* guaiacum reaction has, in all probability, no real significance as such in plant metabolism, but is merely the outcome of the presence of a certain metabolic product.

"*Transmission of Amakebe by means of* Rhipicephalus Appendiculatus, *the Brown Tick.*" By Dr. A. THEILER, C.M.G.

"*Distribution and Action of Soluble Substances in Frogs deprived of their Circulatory Apparatus.*" By S. J. MELTZER.

"*Discrimination of Colour.*" By F. W. EDRIDGE-GREEN, M.D., F.R.C.S.

If a definite portion of spectrum be isolated it will appear monochromatic, the size of the monochromatic region varying with the luminosity and wave-length of the light and the colour perception of the observer.

Lord Rayleigh has expressed the opinion that he can discriminate between the colours in a monochromatic region even to the extent of distinguishing between the colours of the two D lines.

I do not find this possible when special precautions are taken to have a pure spectrum and to avoid the physiological effect of contrast through varying intensities of the areas to be compared.

The monochromatic area may be magnified without altering its monochromatic appearance; the intensity of the light source being increased to compensate for the diminished luminosity. The monochromatic area may also be examined through a double-image prism, or be projected by means of a double-image prism upon a screen, so that the violet side of one area be adjacent to and just touches the red side of the other area. In this way the monochromatic area may be made as large as desired, the intensity of the source of light being increased as required. An arc light gives two very bright areas of colour. This method is the most favourable for the detection of any difference; the monochromatic areas, however, still remain monochromatic.

CHEMICAL SOCIETY.

Ordinary Meeting, May 4th, 1911.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 250).

125. "*Aromatic Antimony Compounds.* Part II. *The Action of the Chlorides of Antimony on Aniline and its Derivatives.*" By PERCY MAY.

The action of antimony trichloride on aniline has been referred to by Schiff (*Comptes Rendus*, 1863, lvi., 1095) and by Leeds (*Am. Chem. Journ.*, 1882, iii., 137), but their observations are meagre and contradictory, so that a more detailed investigation has now been made. Primary aryl derivatives of antimony, such as *p*-aminophenyldichlorostibine, $NH_2 \cdot C_6H_4 \cdot SbCl_2$, do not appear to be produced, but various additive compounds are formed. The following compounds have been isolated by the action of antimony trichloride on the corresponding amines under various conditions: *Trianiline antimony pentachloride*, $SbCl_5 \cdot 3NH_2Ph$; *o-toluidine antimony trichloride*, $SbCl_3, C_7H_7 \cdot NH_2$; *p-toluidine antimony trichloride*, and *p-chloroaniline antimony trichloride*, $SbCl_3, C_6H_4Cl \cdot NH_2$. *m*- and *p*-nitroanilines do not combine with antimony trichloride under the experimental conditions employed.

The above-mentioned compounds dissolve in hydrochloric acid, being thereby dissociated into their constituents. The solutions so obtained yield insoluble crystalline diazo-compounds of the type $R \cdot N_2Cl, SbCl_3$ on treatment with nitrous acid.

Antimony pentachloride reacts violently with aniline, even when both substances are in dilute chloroform solution. It also reacts very vigorously with benzene, toluene, and xylene. In all these cases, partial chlorination of the aromatic compound takes place, the remainder then forming additive products with the antimony trichloride.

126. "*Synthetical Experiments in the Group of the* iso-*Quinoline Alkaloids.* Part I. *Anhydrocotarninenephthalide.*" By EDWARD HOPE and ROBERT ROBINSON.

An account was given of the preparation and properties of anhydrocotarninephthalide, and of a number of its derivatives.

127. "*The Solubility of Electrolytes in Aqueous Solutions.* Part I. *Solubility of Salts in the Corresponding Acids.*" By JAMES IRVINE ORME MASSON.

Determinations have been made at 30° of the solubilities of sodium chloride and of barium chloride in aqueous hydrochloric acid, and of barium nitrate, and of silver nitrate in aqueous nitric acid. The concentrations of acid were such that the solubilities of the salts ranged from 100 per cent to about 3 per cent of the values in pure water.

It has been found that the relation of acid concentration to solubility is well expressed by a simple linear differential equation of the first order. The formula also expresses satisfactorily Engel's results for the solubilities of numerous chlorides in hydrochloric acid at 0° (*Comptes Rendus*, 1886, cii., 619; 1887, civ., 433; *Ann. Chim. Phys.*, 1888, [vi.], xiii., 132).

Study of the specific gravities shows that the molecular volumes of water, acid, and salt in saturated solution are to be regarded as constant in a given case; that is, they are independent of the proportions in which the constituents are mixed. By means of equations embodying this, the specific gravities of the solutions can be calculated with considerable accuracy.

128. "*The Effect of Temperature and of Pressure on the Equilibrium* $2CO \rightleftharpoons CO_2 + C$." By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

In Le Chatelier's general formula for equilibrium in gaseous systems:—

$$500 \int L \frac{dT}{T^2} + (N' - N) \log_e P + \\ + \log_e \frac{C_1^{n_1} \cdot C'_1{}^{n'_1} \cdot \cdot \cdot \cdot}{C_2^{n_2} \cdot C'_2{}^{n'_2} \cdot \cdot \cdot \cdot} = k;$$

the effect of pressure, measured in atmospheres, is given by the expression $(N' - N) \log_e P$. Using a method of experiment at constant volume different from that previously employed by them (*Trans.*, 1910, xcvii., 2182), the authors find that this formula holds for the system $2CO \rightleftharpoons CO_2 + C$ at all pressures between 0·5 and 3 atmospheres for temperatures between 1073° and 1373° Abs. The value of k, however, increases linearly from 19·85 to 20·15 over this range of temperature when the value of L (the total heat of the reaction) is regarded as constant, and equal to

39,000 calories, as in their previous communication. The introduction of a value $L_T = L_0 + 2{\cdot}02T - 0{\cdot}0031T^2$, calculated from the difference between the molecular heats at constant volume of the factors and products of the system, gives the constant a permanent value, 18·74, L_0 (the total heat of the reaction at absolute zero) being calculated as equal to 38,055 calories.

Le Chatelier's equation therefore becomes, for the system under consideration :—

$$\tfrac{1}{2}\cdot\frac{38{\cdot}055 + 2{\cdot}02T - 0{\cdot}0031T^2}{T} + \log_e P + \log_e \frac{C_{CO}}{C_{CO_2}} = 18{\cdot}74,$$

from which the percentage of carbon dioxide and carbon monoxide in equilibrium over excess of carbon can be calculated for any temperature and pressure.

The rate of attainment of equilibrium is extremely slow at temperatures below 1073° Abs.

129. "*Nitrites of the Benzylammonium Series : Benzylammonium Nitrite and Dibenzylammonium Nitrite, and their Sublimation and Decomposition by Heat.*" By Prafulla Chandra Ray and Rasik Lal Datta.

By the interaction of silver nitrite and mono- and dibenzylamine hydrochlorides respectively in aqueous solution, and evaporation in a vacuum of the filtrate, the corresponding nitrites are obtained. The nitrites of this series are more stable than the corresponding ones of the aliphatic series.

130. "*The Conductivity and Viscosity of Aqueous Solutions of Aniline Hydrochloride at 25°.*" By Nevil Vincent Sidgwick and Bernard Howell Wilsdon.

These properties were measured for solutions from N/10 to more than 4N. With increasing concentrations the product of conductivity and viscosity first falls, reaching a minimum at about 2N, and then remains nearly constant, with a slight tendency to rise. The product of the conductivity and the two-thirds power of the viscosity falls continuously.

131. "*The Solubility of Aniline in Aqueous Solutions of its Hydrochloride.*" By Nevil Vincent Sidgwick, Percival Pickford, and Bernard Howell Wilsdon.

Aniline is miscible in all proportions with water at 168°, and with 4·5N-hydrochloric acid at 30°. The authors have measured the solubility in solutions of various strengths, at temperatures up to complete miscibility. They have also determined at 25° the partition-coefficient (concentration in water/concentration in aniline) of the salt between the two layers. This falls rapidly with increasing concentration, being 20 for a N/10- (aqueous) solution, and 0·9 for a 1·3N-solution. The bearing of this on the shape of the solubility curves was discussed.

Some measurements have also been made of the conductivity and viscosity of solutions of the hydrochloride in mixtures of aniline and water. The results appear to indicate that the conductivity for a given concentration of salt is proportional to the amount of water in the solvent.

132. "*Some Reducing Actions of Mercury.*" By David Borar.

The action of mercury on solutions of a number of substances has been examined with the following results :—

1. Potassium permanganate is reduced to potassium hydroxide and manganese dioxide, the mercury being oxidised to mercuric oxide.

2. Potassium dichromate in neutral solution is not reduced. In the presence of hydrochloric acid, however, chromium chloride and mercurous chloride are formed.

3. Ferric salts in the presence of hydrochloric acid are reduced to the ferrous state. The experiments showed that mercury may be used as reducing agent for ferric compounds in the estimation of iron.

4. Potassium persulphate is reduced to potassium sulphate, the mercury being converted into a basic sulphate.

5. Copper sulphate in the presence of hydrochloric acid is reduced to cuprous chloride.

6. Nitrobenzene in the presence of hydrochloric acid is reduced to aniline to a small extent.

7. Solutions of potassium nitrate, potassium chlorate, and sodium peroxide are not acted on by mercury to any appreciable extent.

133. "*Note on the Preparation of β-Hydrindone.*" By Jocelyn Field Thorpe.

In a previous paper (Moore and Thorpe, *Trans.*, 1908, xciii., 165) a process was described by which *o*-phenylenediacetonitrile, which is derived from *o*-xylylene dibromide by the action of potassium cyanide, could be quantitatively transformed into β-imino-α cyanohydrindene by the action of sodium ethoxide, thus :—

$$C_6H_4{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CH_2{\cdot}CN\\CH_2{\cdot}CN\end{matrix} \rightarrow$$

$$\rightarrow C_6H_4{<}\begin{matrix}-CH_2-\\CH(CN)\end{matrix}{>}C{:}NH.$$

It was also shown that β-imino-α-cyanohydrindene could be converted, through the corresponding carboxylic acid, into β-hydrindone :—

$$C_6H_4{<}\begin{matrix}-CH_2-\\CH(CO_2H)\end{matrix}{>}C{:}NH \rightarrow C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CO.$$

Since that time it has been found that β-imino-α-cyanohydrindene can be directly converted into β-hydrindone by a much simpler process, and, as the yield by the newer method is 90 per cent of the theoretical, the preparation of this ketone from *o*-xylene is now an easy matter.

Twenty grms. of β-imino-α-cyanohydrindene are dissolved in 50 cc. of cold concentrated sulphuric acid, and the clear solution is kept at the ordinary temperature for one hour. It is then poured into six times its volume of water, and distilled in a current of steam, a large flask being used for the purpose, as much frothing occurs. β-Hydrindone passes over with the steam, and solidifies in the receiver.

The *semicarbazone* of β-hydrindone, which does not appear to have been prepared previously, separates as a white precipitate when a solution of semicarbazide hydrochloride in aqueous sodium acetate is added to a solution of the ketone in dilute alcohol. It crystallises from hot absolute alcohol, in which it is only sparingly soluble, as slender needles, which melt and decompose at 218° :—

0·1803 gave 0·4209 CO_2 and 0·0904 H_2O. C = 63·66; H = 5·57.

$C_{10}H_{11}ON_3$ requires C = 63·5 ; H = 5·8 per cent.

In the previous paper (*loc. cit.*, p. 174) it was stated that β-hydrindone prepared by this method does not alter on keeping, and it was suggested that the unstable character of this compound when prepared by other methods must be due to the presence of some impurity. This statement was written after the ketone had been under observation for three to four months prior to the publication of the paper. A specimen of β-hydrindone prepared by this method was found, however, to have been completely transformed into a brown viscid resin after having been kept in a well-stoppered bottle for eighteen months.

PHYSICAL SOCIETY.

Ordinary Meeting, May 12th, 1911.

Prof. H. L. Callendar, F.R.S., President, in the Chair.

Diagrams of Stream Lines past an Elliptic Cylinder were exhibited by Sir George Greenhill and Col. R. L. Hippisley.

The stream lines ψ = constant, and the orthogonal curves ϕ = constant, are drawn on Weir's azimuth diagram, ruled into elliptic co-ordinates ξ and η instead of the Cartesian x and y of squared paper. These are connected by ;—

1. $z = c \cosh \zeta$, where $x = z + iy$ and $\zeta = \xi + i\eta$.

Further write :—

2. $w = \phi + i\psi = m \cosh (\zeta - \gamma)$, where $\gamma = \alpha + i\beta$, which gives—

3. $\phi = m \cosh (\eta - \alpha) \cos (\xi - \beta)$, $\psi = m \sinh (\eta - \alpha) \sin (\xi - \beta)$, so that $\psi = 0$ over the ellipse $\eta = \alpha$ and along the hyperbola $\xi = \beta$. Also $m = Q(a + b)$, where Q is the velocity at infinity, and a, b are the semi-axes of the fixed ellipse.

The system is a generalisation to confocal ellipses of the curves in Maxwell's Fig. XV., and their oblique trajectories shown in Fig. XVI., and it may be interpreted electrodynamically in the same manner as in Maxwell's "Electricity and Magnetism," §§ 434, 436.

A linkage of Peaucellier cells for drawing the curves of Maxwell's Fig. XV. was shown by Col. Hippisley.

Discussion.

Dr. A. RUSSELL appreciated keeping the increments of ξ constant in the diagrams, so that the velocities could be seen at a glance.

Prof. C. H. LEES remarked that in a paper by Hele Shaw and A. Hay about ten years ago a diagram was given of the magnetic lines of force past an elliptic cylinder for which $\mu = 8$.

Sir GEORGE GREENHILL, in reply, said that the curves in Hay's paper were the oblique trajectories of those now shown.

A paper on "*The Method of Constant Rate of Change of Flux as a Standard for Determining Magnetisation Curves of Iron*," by J. T. MORRIS and T. H. LANGFORD, was read by Prof. J. T. Morris.

The research described was instituted with the object of finding what differences there were between the magnetisation curves for a given sample of iron when determined (1) by the older methods in which the flux is changed suddenly, (2) by a method in which it is changed exceedingly slowly and at a uniform rate.

The methods experimentally examined were :—

1. Method of constant rate of change of flux.
2. "Slow cyclic" hysteresis loops by Method 1.
3. "Step by step" magnetisation curve.
4. "Step by step" hysteresis loops.
5. Method of reversals.
6. Alternating-current magnetisation curve.

Details are given of the theory and practical working of Method 1. In this method the magnetising current is continuously increased through a primary winding by a specially designed resistance at such a varying rate as to maintain a constant voltage generated in a secondary winding. A certain amount of skill is required in operating the resistance, but an average experimenter may easily acquire this with a little practice. The complete change of the current occupied times varying from one up to some five minutes.

Tables are given of the magnetisation curve determined by the six different methods at a number of values from H 0·3 up to 70·0, and of the permeability from B 500 up to 17,000.

At low values of the magnetising force the uniformly varying flux method gives results of some 200 lines per square centimetre in excess of the older methods.

As regards the time required for determinations by the various methods experimentally examined, ballistic methods are undoubtedly the most tedious. The alternating-current method (Method 6) has considerable advantages in this respect, a full set of readings of magnetising current and induced voltage occupying a very short time. When, however, it is necessary to take oscillograms at various points in order to plot curves of form factors, the time required is enormously increased. The method of uniformly-varying flux (Method 1) is peculiarly adapted for use where time is a consideration, and at the same time a high degree of accuracy is desired. A complete magnetisation curve may be taken in a very few minutes, and the mean of many such curves obtained in, say, one hour, the iron being demagnetised between each test.

The method of "uniformly varying flux" appears to possess advantages, both scientific and practical, over the older methods in use for the testing of ring samples of magnetic materials. It avoids difficulties due to eddy currents and magnetic viscosity, which effects are themselves due primarily to rapid or irregular changes of flux. Besides rapidity of experiment it also has the advantage of accuracy of repetition under standard or predetermined conditions of magnetic change.

The method is therefore commended for the carrying out of magnetic tests, especially where great accuracy under definitely known conditions of experiment are essential.

Discussion.

Mr. A. CAMPBELL remarked that it was rather difficult to say whether it was tests made with a slowly varying flux that were required in practice. He thought tests made with cyclical changes were more useful. The differences in the results given by the two methods were important. He pointed out that the method could be used for the determination of the ohm by substituting a known mutual induction for the iron under test.

Dr. A. RUSSELL pointed out that the value of H was different at the inner and outer radii of the iron ring used by the authors.

Dr. S. W. J. SMITH said it would have been interesting and instructive if the authors had performed a similar series of experiments by the different methods upon some material freer from magnetic viscosity than soft iron. Experiments made upon a sample of nearly pure iron in weak fields did not seem to be explicable along the lines suggested by the authors for the iron they used.

Prof. C. H. LEES drew attention to the extraordinary simplicity of the reluctivity curves. It looked as if $1/\mu$ were a linear function of H

The PRESIDENT remarked that by superposing on the constant magnetising field an alternating field which was gradually reduced to nothing, much larger values of the apparent permeability were obtained. For weak fields it was over 100,000. This effect was due to the residual magnetism left by the alternating field.

Prof. J. T. MORRIS, in reply, stated that they had not tried their method at widely different speeds. In reply to Dr. Russell, he stated that the same iron ring was tested by the different methods. Replying to Mr. Campbell, he had thought of the present method as a means of measuring a mutual induction.

The PRESIDENT gave a demonstration of the action of the Electric Thermo-regulator designed by him for experiments by the continuous electric method on the specific heat of water in 1897, and described in the *Phil. Trans.*, A, 1902. The expansion of liquid in a bulb causes a thread of mercury to make contact with a platinum wire actuating a relay which puts a 16 c.p. lamp in series with a 32 c.p. lamp in the regulator tank. If the wire is fixed, hunting occurs, owing to the mercury sticking to the wire and to lag of the regulator bulb. This is prevented, either by causing the wire to move up and down continually through a distance of about 1 mm. with a period of five to ten seconds, or by fixing the lamp bulb close to the regulator bulb. The hunting was demonstrated by means of a platinum thermometer reading to 0·001° C. Other details of construction were also explained. The same type of regulator is now being employed for measurements of the variation of the specific heat of water by a new method in which two steady currents at different temperatures are allowed to mix, or share their heat, the resulting temperature being observed.

CORRESPONDENCE.

THE RELATION BETWEEN MOLECULAR VOLUMES AND VALENCY NUMBERS.

To the Editor of the Chemical News.

Sir,—In the Chemical News of April 28th (vol. ciii., p. 203), Mr. Edw. E. Price refers to an article by Prof. Pope, F.R.S., in which a table of calculated molecular volumes of the normal paraffins at the melting-point appeared, and which was used as evidence in favour of the close connection between valency and volume.

The table in question forms part of one which I have given as illustrating the significance of molecular volumes from the point of view of Kopp. I am, of course, responsible for the matter in question, and thus would ask you to kindly grant me the space in which to deal with one or two points raised by the letter.

For the manner in which the constant 2·970 was obtained I must refer Mr. Price to Dr. Smiles' "The Relations between Chemical Constitution and Physical Properties." An elaborate discussion of the best relation for representing the facts will be found in the original papers (*Trans. Chem. Soc.*, 1907, xci., 112; *Phil. Mag.*, 1907, [6], 14; Chemical News, 1908, xcviii., 85).

Mr. Price, who seems to object to the general method used, need not be reminded that it is the one generally adopted in dealing with physical properties which are nearly or even only approximately additive, *e.g.*, molecular refractions, capillary constants, molecular critical coefficients, &c.

Doubtless the selection of *suitable* constants is always permissible, but they should have a natural and not a strained relation to the facts. The constant given in the letter, viz., 1·285, which is the reciprocal of the mean density or the volume occupied by 1 grm. of the compound, is *not suitable*, and molecular volumes *cannot* be calculated by means of the molecular weights. This the following table shows:—

The Calculation of Molecular Volumes by means of Molecular Weights and the Valency Numbers.

Compound.	M.W.	W.	M.V.	V calculated for M+*v*.	Δ.	V calculated =WS.	Δ.
$C_{13}H_{28}$	184	80	237·3	236·4	−0·9	237·6	+0·3
$C_{14}H_{30}$	198	86	255·4	254·4	−1·0	255·4	—
$C_{15}H_{32}$	212	92	273·2	272·4	−0·8	273·2	—
$C_{21}H_{44}$	296	128	380·3	380·3	—	380·2	−0·1
$C_{31}H_{64}$	436	188	558·4	560·2	+1·8	558·4	—
$C_{32}H_{66}$	450	194	576·2	578·2	+2·0	576·2	—
$C_{35}H_{72}$	492	212	629·5	632·2	+2·7	629·6	+0·1

The ratios for $C_{13}H_{28}$ and $C_{35}H_{72}$ are—

$$\frac{V_2}{V_1} = 2{\cdot}650\,\frac{W_2}{W_1} = 2{\cdot}652\,\frac{M.W_2}{M.W_1} = 2{\cdot}674.$$

These facts speak for themselves. Moreover, the constants (?) for other series, taking the molecular weight as the basis of computation, are:—For the higher alcohols, 1·223; the ketones, 1·244; the fatty acids, 1·098; and the nitriles, 1·198.

The molecular volumes, on the other hand, will be found to be very nearly proportional to the aggregates, W, of integral numbers, W_1, while the constant is 2·970 in all the series.

The interesting point raised by Mr. Price in connection with the relation between the alternating character of some volume differences for CH_2 with the well-known alternating character of the melting-point in some series, I hope to deal with, with your kind permission, in an early number of the Chemical News.—I am, &c.,

Gervaise Le Bas.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliı., No. 13, March 27, 1911.

Metallography of the System Gold-tellurium.—Maurice Coste.—When gold and tellurium are fused together in different proportions in exhausted quartz tubes a compound, $AuTe_2$, is formed. Margottet's compound, Au_2Te, does not exist.

Two New Compounds of Stannous Chloride and Ammonia. Ath. I. Sofianopoulos.—Ammonia is absorbed by stannous chloride at temperatures below 0°, a compound, $SnCl_2.2NH_3$, being formed, which is stable at the ordinary temperature. It is a yellow amorphous powder with an ammoniacal smell. When exposed to the action of air it blackens, and is decomposed by the water in the air, $SnCl_2.2NH_3 + H_2O = SnO + 2NH_4Cl$. At a temperature of about 300° stannous chloride absorbs ammonia, forming a new compound, $3SnCl_2.2NH_3$. It is a red-brown double refracting mass, which appears to be the most stable of the compounds of stannous chloride and ammonia. It is decomposed by water as follows:—$3SnCl_2.2NH_3 + H_2O = 2SnCl_2 + SnO + 2NH_4Cl$. With hydrogen it yields metallic tin.

Preparation of Arsenic Amalgam.—E. Dumesnil.—The reduction of a mixture of solutions of arsenious acid and mercury bichloride by hypophosphorous acid gives arsenic amalgam, As_2Hg_3. If the mercury salt is present in excess a mixture of the amalgam and mercury is obtained, and may readily be separated into its constituents owing to their different densities. When heated arsenic amalgam volatilises, giving a sublimate of very small amounts of arsenious anhydride, and arsenic and mercury.

Decomposition of Metallic Xanthates by Heat.—Alexandre Hérbet.—Metallic xanthates give gaseous and liquid products when heated. The gases consist chiefly of sulphuretted hydrogen, carbon dioxide, and a small quantity of combustible gases. The liquids obtained from the xanthates of K, Ba, Fe, Co, &c., include carbon bisulphide and oxysulphide, alcohol, ethyl mercaptan, and ethyl, mono, and disulphide, while the xanthates of Ni, Ag, Cu, and Hg give ethylxanthate of ethyl, $C_2H_5O.CS.SC_2H_5$.

Action of Water-vapour on Carbon in presence of Lime.—Léo Vignon.—At a high temperature water acts on carbon according to the following equation:—$C + H_2O = CO + H_2$. This is an endothermic reaction, and is accompanied by the absorption of 29·1 cal. At 600—800° water-vapour acts on an intimate mixture of carbon and chalk, giving the following reactions:—

$$C + CaO + 2H_2O = CaCO_3 + 2H_2,$$
$$2C + CaO + 2H_2O = CaCO_3 + CH_4,$$
$$3C + CaO + 2H_2O = CaCO_3 + C_2H_4.$$

These reactions are exothermic, the amounts of heat disengaged being 25 cal., 47 cal., and 17 cal. respectively.

Temperature of Action of Alkali Metals on Water.—L. Hackspill and R. Bossuet.—The alkali metals react with water at about −100°, the exact temperatures being—For cæsium, −116°; rubidium, −108°; potassium, −105°, sodium, −98°. Probably it is water-vapour and not ice which reacts on the metals.

Preparation of True Acetylenic Alcohols.—M. Lespieau.—True acetylenic alcohols which possess a hydroxyl group next to two doubly bound carbon atoms can be prepared by condensing monobrom acroleïn with methyl magnesium bromide, and treating the brom-

ethylenic alcohol obtained with potash. The alcohols, $CH_2=CH—CHOH—R$, can be used instead of acroleïn.

Catalytic Hydrogenation of Cyclopentanone.—M. Godchot and F. Taboury.—In presence of reduced nickel cyclopentanone is converted by hydrogen at 125° into cyclopentanol, some cyclopentane being also formed, and a product of the formula $C_{10}H_{16}O$. Apparently two molecules of cyclopentanone give up one molecule of water, giving rise to an unsaturated ketone. This, then, fixes two atoms of hydrogen, yielding α-cyclopentylcyclopentanone.

MISCELLANEOUS.

Conversion of Stable Isomers into Labile Form by Ultra-violet Light.—R. Stoermer.—With the exception of crotonic acid all the numerous ethylene derivatives investigated by the author could be converted into the labile form by the action of the radiation of a quartz lamp. By this method many hitherto unknown allo-forms of unsaturated acids could be prepared, *e.g.*, that of *o*-chlorcinnamic acid, and it was found that cumarin acid is the allo-form of *o*-cumaric acid.—*Berichte*, xliii., No. 5.

Cleaning Discoloured Marble.—F. P. Dunnington.—Frequently when marble is exposed, as in a cemetery, where it is more or less sheltered by trees, it is disfigured by lichens and other vegetable growth. In many instances this growth has died and become brown or black in colour. All such discolorations may be readily removed by soda lye of moderate strength, about 5 per cent. That which is rotted is dissolved, and the remainder is soon disintegrated. The following directions answer well:—A box of concentrated lye, containing about twelve ounces of caustic soda, is dissolved in a two-gallon bucket of water. Spread this over the stone with a small cheap scrubbing brush, made with vegetable fibre, preferably provided with a handle so as to avoid getting the lye upon the hands, the clothes, or the shoes. After ten minutes or more pour water over the stone to wash off most of the lye and then rub it a little with the brush, using some sand if necessary, and the stain will be removed. Of course this liquid has no effect upon the stone itself, and is most easily washed away. So far as the wash falls upon the ground it will improve rather than harm any grass or other plants. Should the lye remain upon the skin it may occasion an ugly sore. If splashed upon the clothing the prompt application of a solution of sal ammoniac will prevent corrosion of the goods. — *Chemical Engineer*, Chicago, February, 1910.

Annual Tables of Constants and Numerical Data Chemical, Physical, and Technological. — At the International Congress of Applied Chemistry held in London in 1909 an International Commission was appointed for the purpose of compiling and publishing Annual Tables of Constants and Numerical Data; and this Commission was subsequently accorded the patronage of the Association of Academies at the meeting of that body held in Rome in 1910. According to the programme drawn up by the Commission the Tables published in any one year are intended to contain all the numerical data likely to be of interest in connection with Chemistry, Physics, and allied Sciences, pure and applied, to be found in the literature published during the previous year. The data are to be accompanied by full bibliographic references. This programme has now (May, 1911) so far matured that portions of the volume for 1910 are already in the press, while the manuscript of the remaining portions is approaching completion. Owing to the immense volume of scientific and technical literature which is continually being produced, the difficulties in the way of finding out whether any given measurement has been made or not are increasing year by year. Existing systems of indexing and abstracting offer only limited help, since a large number of measurements are made in the course of researches to which they are purely subsidiary, so that their existence cannot be inferred from the titles and subtitles of the papers in which they are recorded. Also Tables which appear only at long intervals, such as those of Landolt and Börnstein, can of necessity cover only a small part of the ground; and, moreover, in most cases they are hampered by the limitations of private enterprise. The Annual Tables should therefore fill a serious gap which has hitherto existed in the systematic indexing of scientific and technical results. It is hoped that ultimately the enterprise may become self-supporting; but obviously this cannot be the case for some time to come. The Commission has been greatly assisted by grants from various societies; for example, in this country, from the British Association, Chemical Society, Faraday Society, Royal Dublin Society, Royal Irish Academy, Royal Society of Edinburgh, and the Society of Chemical Industry. Donations have also been received from a few private persons, notably from the Right Hon. the Earl of Berkeley, F.R.S. The financial position is, however, still far from satisfactory; and further help from societies and private donors is urgently needed. In this connection it may be mentioned that neither the General Secretary nor the Members of the Commission receive payment for their services, except in so far as they may perform actual compiling or abstracting. The organisation of the Commission is sufficiently complete to deal effectively with the periodical literature, but it happens occasionally that data are published only in non-periodical publications, such as books or monographs; and such data may easily be overlooked. Accordingly, in order that the Annual Tables may be as complete as possible, the authors of such books, monographs, &c., are requested to communicate with one or other of the Members of the Commission. In cases where the data are numerous, specimen copies or corrected proofs of the tables containing the data would be very acceptable. The Members of the International Commission for the United Kingdom are:—Dr. Alex. Findlay, the University, Edgbaston, Birmingham; Dr. R. T. Glazebrook, C.B., F.R.S., the National Physical Laboratory, Teddington, Middlesex; and Dr. N. T. M. Wilsmore, University College, Gower Street, London, W.C. The General Secretary is Dr. Charles Marie, 98, Rue du Cherche-Midi, Paris VI.

NOTES AND QUERIES.

"*" Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"Bazaar Medicine of India"—Can any reader supply name of author, publisher, and price of this book.—J. C. T.

MEETINGS FOR THE WEEK.

TUESDAY, 6th.—Royal Institution, 3. "Charnwood Forest and its Fossil Landscape," by W. W. Watts, F.R.S.

THURSDAY, 8th.—Royal Institution, 3. "Practical Progress in Wireless Telegraphy," by T. Thorne Baker, F.C.S.

FRIDAY, 9th.—Royal Institution, 9. "Applications of Physical Chemistry to the Doctrine of Immunity," by Prof. Svante Arrhenius, Hon.F.R.S., &c.

—— Physical Society, 8. "The Lüders Lines on Mild Steel," by W. Mason. "Tables of Circular and Hyperbolic Functions for Complex Values of the Argument," by A. Johnstone. "Measurement of Contact Differences of Potential," by Prof. Anderson and J. G. Bowen. "New Method of Approximate Harmonic Analysis by Selected Ordinates," by S. P. Thompson. Exhibition of a model illustrating the Passage of a Light Wave through Quartz, by H. S. Allen. Exhibition of Gyroscopic Apparatus, by Sir G. Greenhill.

SATURDAY, 10th.—Royal Institution, 3. "Types of Greek Women," by W. L. Courtney, M.A.

THE CHEMICAL NEWS

Vol. CIII., No. 2689.

A NEW METHOD OF CHEMICAL ANALYSIS.*

By Prof. Sir J. J. THOMSON, M.A., LL.D., D.Sc., F.R.S.

I have had on several occasions the privilege of bringing before the members of the Royal Institution some of the results of the experiments on the positive rays on which I have been engaged for the last few years. I wish this evening to direct your attention to some applications of these to various chemical problems.

The first application I shall consider is the use of these rays to determine the nature of the gases present in a vacuum tube, to show how they can be used to make a chemical analysis of these gases—an analysis which, as we shall see, will enable us to determine not merely whether an element, say, for example, oxygen, is present in the tube, but will tell us in what form it occurs, whether, for example, it is present in the atomic as well as the molecular condition, and whether there are allotropic modifications present, such as ozone, O_3, and other still more complex aggregations.

The method is as follows:—The positive rays after passing through a fine tube in the cathode are exposed simultaneously to magnetic and electric forces, the magnetic field being arranged so as to produce a vertical deflection of the rays, while the electric field produces a horizontal deflection. Thus, if when neither electric nor magnetic fields are present, the rays strike a screen placed at right angles to their direction at a point O, they will, when both electric and magnetic forces are at work, strike it at a point P, where the length of the vertical line P N is equal to the deflection produced by the magnetic field, and the horizontal line O N to that produced by the electric field.

We know from the theory of the action of electric and magnetic fields on moving electrified particles, that—

$$PN = A\frac{e}{mv} \qquad ON = B\frac{e}{mv^2},$$

where A and B are constants depending on the strength of the magnetic and electric fields and the geometrical data of the tube, e is the charge on the particle, m its mass, and v its velocity.

From these relations we see that—

$$\frac{m}{e} = \frac{A^2}{B}\frac{ON}{PN^2}.$$

When these rays strike against a photographic plate, they affect the plate at the point against which they strike, and thus when the plate is developed we have a permanent record of the deflections of the rays. The methods of taking these photographs and the details of the experiment are described in my paper in the *Philosophical Magazine*, February, 1911. The values of A and B can be determined accurately by the methods I have given in previous papers, and hence if we measure on the photographs the values of O N and P N, we can determine the value of m/e. If we wish to compare the values of m/e for two different rays, it is not necessary to determine A and B, all we have to do is to measure the values of O N and P N; and thus the photograph alone gives us the means of comparing the value of m/e.

Since for the same type of carrier m/e is constant, so that whatever may be the velocity $\frac{PN^2}{ON}$ is constant, and therefore the locus of P, *i.e.*, the curve traced on the photographic plate by this carrier, is a parabola. The reason we get a curve instead of a point is that the rays are not all moving with the same velocity, and the slower ones suffer greater deflection than the quicker ones. Each type of carrier produces its own line on the plate, and there are as many curves on the plates as there are kinds of carriers; from an inspection of the plates we can find not merely the number of kinds of carriers, but from the dimensions of the curves we can at once determine the atomic weight of the carrier, and thus determine its nature. This is one of the great advantages of this method. To illustrate this advantage, let us compare the method with that of spectrum analysis. If the spectroscopist observes a line unknown to him in the spectrum of a discharge tube, the most we can deduce without further investigation is that there is some unknown substance present in the tube, and even this would be doubtful, as the new line might be due to some alteration in the conditions of the discharge. But if we observe a new curve in the positive ray spectrum, all we have to do is to measure the curve and then we know the atomic weight of the substance which produced it. To take an example, I have photographed the positive ray spectrum for nitrogen prepared from the atmosphere, and that for nitrogen prepared from some nitrogenous compounds, and have found that the former contains a line which is not in the latter, and that the value of m/e for this line is forty times that for the atom of hydrogen. (As a matter of fact, there is a second very faint line for which m/e is about twenty times that for the atom of hydrogen. This is probably due to an atom of argon with two electric charges). We thus know that atmospheric nitrogen contains an element of atomic weight 40, which is not present in chemical nitrogen—this element is, of course, argon. We might, by ordinary spectrum analysis have found lines in the spectrum of atmospheric nitrogen which are not in the spectrum of chemical nitrogen, and might thus have suspected the presence of another element, but spectrum analysis could not tell us anything about the nature of this element, whereas the positive ray spectrum at once gives us its atomic weight.

The positive-ray method is even more delicate than that of spectrum analysis, for by it we can detect the presence of quantities of a foreign gas too minute to produce any indication in the spectroscope. I have, for example, often been able to detect the presence of helium by this method, when no indication of its presence could be detected by a spectroscope.

Again, when a line in the positive-ray spectrum can be seen, the atomic weight of the carrier which produces it can be determined with great accuracy. Though the method is only a few months old, it is even now sufficiently developed to determine with an accuracy of 1 per cent the atomic weight of a gaseous substance, without requiring more than 1/100 mgrm. of the substance. Another very important advantage of this method is that it is not dependent upon the purity of the material; if the material is impure the impurities merely appear as additional lines in the spectrum, and do not affect the parabola due to the substance under examination, and therefore produce no error in the determination of the atomic weight. The method would seem to be peculiarly suitable for the determination of the atomic weights not merely of the emanation from radio-active substances, but also those of the products into which they disintegrate.

The rays, too, are registered within less than a millionth of a second after their formation, so that when chemical combination or decomposition is occurring in the tube, the method may disclose the existence of intermediate forms which have only a transient existence, as well as of the final product, and may thus enable us to gain a clearer insight into the process of chemical combination.

I will now show a few slides prepared from the photographs we have taken of the positive-ray spectra. The first (Fig. 1) is that of nitrogen prepared from air; the measurements of the photograph showed that the atomic weights of the carrier producing these curves were as follows:—

* A Discourse delivered before the Royal Institution, April 7th, 1911.

Positive.		Negative.
1	$H+$	1 $H-$
1·99	H_2+	11·20 $C-$
6·80	$N++$	15·2 $O-$
11·40	$C+$	—
13·95	$N+$	—
28·1	N_2+	—
39	$Arg+$	—
100	$Hg++$	—
198	$Hg+$	—

The symbol $H+$ denotes that the carrier is an atom of hydrogen with one charge; H_2+ that it is a molecule of hydrogen with one charge; $N++$ that it is an atom of nitrogen with two charges; and so on.

With nitrogen from NH_4NO_2 the lines were as follows (the magnetic force was so large that some of the lines corresponding to the lighter particles were thrown off the plate):—

6·1	$C++$	44·2	CO_2+
7·02	$N++$	65·5	$Hg+++$ (?)
12·08	$C+$	100	$Hg++$
14·01	$N+$	204	$Hg+$
27·9	N_2+		

The next slide (Fig. 2) is the positive-ray spectrum for CO, and again the magnetic field is so great that the lighter carriers do not appear.

From the measurement of the lines we find that the atomic weight of the carrier is:—

Positive.		Negative.
6·00	$C++$	12 $C-$
6·95	$N++$	16 $O+$
7·95	$O++$	—
12·02	$C+$	—
13·9	$N+$	—
15·95	$O+$	—
28·05	$CO+$	—
43	CO_2+	—
69·5	$Hg+++$ (?) very faint	—
100	$Hg++$	—
202	$Hg+$	—

The spectrum for CO_2 is represented in Fig. 3; the atomic weights are:—

5·98	$C++$	43·9	CO_2+
8·00	$O++$	62·5	$Hg+++$ (?) very faint
12·00	$C+$	99·6	$Hg++$
16·00	$O+$	200·0	$Hg+$
28·02	$CO+$		

The spectrum of CH_4, of which a small region with five lines close together, is shown in Fig. 4. This is interesting, because the measurement of these lines shows that their atomic weights are 12, 13, 14, and 15, 16, and thus that we have here, C, CH, CH_2, CH_3, CH_4. If I am not mistaken, this is the first occasion when the atoms, CH, CH_2, CH_3, have been observed in a free state.

The spectrum of the analogous compound chloroform, $CHCl_3$, is represented in Fig. 5. The atomic weights represented in this are:—

1	$H+$	18·5	$Cl++$
1·5	(?)	27·7	$CO+$
2	H_2+	36	$Cl+$
3	(?)	46·5	$CCl+$
6	$C++$	63	(?) faint
8	$O++$	81	CCl_2
11·9	$C+$	102	$Hg++$
13·7	$N+$	201	$Hg+$
16	$O+$		

The carriers with atomic weights 1·5 and 3 have not been identified. They are of frequent occurrence. I have here two slides, one of SiH_4 (Fig. 6), and the other of the residual gas in the tube, in which they are well marked, though at their best they are only faint lines. In Fig. 7 we have the positive ray spectrum of air, taken under conditions which produce very narrow lines, which can be accurately measured.

Let us now consider some of the results brought to light by these photographs. In the first place, they show that a gas through which an electric discharge is passing is a much more complex thing than a collection of molecules all equal to each other. Even an elementary gas becomes in these circumstances a mixture of a great many different substances. Thus, to take oxygen as an example, the photographs show that when a current of electricity passes through it, we may have present simultaneously oxygen in the following states:—

1. Ordinary molecular oxygen, O_2.
2. Neutral atoms of oxygen, O.
3. Atoms of oxygen with 1 positive charge, $O+$.
4. Atoms of oxygen with 2 positive charges, $O++$.
5. Atoms of oxygen with 1 negative charge, $O-$.
6. Molecules of oxygen with 1 positive charge, O_2+.
7. Ozone with a positive charge, O_3+.
8. O_6 with a positive charge, O_6.

And, in addition, there are free negative corpuscles. Thus in the elementary gas there are at least nine (the list has no claim to be exhaustive), separate substances present when the discharge passes through it. Each of these substances has almost certainly different properties, possibly a characteristic spectrum. If we took any other gas we should find that the same thing would be true; thus in hydrogen we have H, H_2, $H+$, $H-$, H_2+, even if we do not ascribe to hydrogen the lines giving $m/e = 1·5$ or 3. In nitrogen we have N, N_2, $N+$, $N++$, N_2+, carbon occurs as $C+$, $C++$, $C-$, chlorine as Cl, Cl_2, $Cl+$, $Cl++$, and $Cl-$, mercury as Hg, $Hg+$, $Hg++$, and probably as $Hg+++$, as there is a very persistent line for which m/e is about 66.

Thus whenever the electric current passes through a gas, and probably whenever a gas is ionised, the gas becomes a mixture of many different substances. We can thus readily understand why in the spectra of many elements many of the lines may be grouped together so as to form different series—the principal series, the first co-ordinate series, and so on—and the spectrum of the discharge-tube regarded as the superposition of a number of different spectra the relative intensities of which may be subject to very great variations. This, indeed, is just what would happen if some or all of the substances which are present when the gas is in the ionised state gave rise to different spectra.

Another feature which I think is of great interest from the point of view of the theory of chemical combination is the occurrence of particles with negative charges. Let us consider for a moment how these are formed. They are formed after the particles have passed through the cathode; the path between the cathode and the photographic plate contains abundance of corpuscles produced by the ionisation of the gas; a neutral particle after passing through the cathode picks up a negative corpuscle, and so becomes negatively charged. For this to occur the attraction between the corpuscle and the neutral particle must be exceedingly strong, for it is not a question of a particle at rest attracting to itself a negatively electrified corpuscle sauntering about in its neighbourhood. In our case the neutral particle is rushing past the corpuscle with a velocity of the order of 10^8 cm. per sec. In order that the particle may in these circumstances be able to drag the corpuscle along with it the attraction between the two must be so great, that to move a corpuscle against this attraction from the surface of the particle away to an infinite distance must require an amount of work of the same order as tha required to communicate to the corpuscle a velocity o 10^8 cm. per sec.; this is equal to the work required to move the atomic charge against a potential difference of about 3 volts, and is therefore comparable with the work required to dissociate some of the most stable chemical compounds.

The fact, then, that some particles get negatively charged shows that in the neutral state these particles have an exceedingly strong affinity for a negatively electrified particle, while the absence of a particular particle from the negative side shows that its affinity is much less, but does not imply that it vanishes altogether. From what we have said, it should follow that the more slowly the neutral particles are moving relatively to the corpuscles, the more easily will the negatively electrified systems be formed. This is confirmed in a very striking way by our experiments, for when the discharge is passing very easily through the tube, and the velocity of the neutral particles is relatively small, the number of negatively electrified particles is very much increased; indeed, in some cases the brightness of the part of the photograph corresponding to the negative particles is as great as that corresponding to the positive, whereas when the discharge is passing with great difficulty, and the velocity of the neutral particles is very high, the negative part is very faint compared with the positive.

The particles which have been observed on the negative side are the hydrogen atom, the carbon atom, the oxygen atom, and the chlorine atom. The presence of oxygen and chlorine atoms might, perhaps, have been expected, as these are universally regarded as strong electro-negative elements, *i.e.*, as elements which have a strong affinity for negative electricity. The presence of the hydrogen atom is more remarkable, for hydrogen is generally considered to be a strongly electro-positive element, yet on these photographs we find it more persistently on the negative side than any other particle; often when no other line on the negative side is strong enough to be detected, the line corresponding to the hydrogen atom is distinctly visible. This is all the more remarkable, because the hydrogen atom, being the lightest of all the particles, is moving with the greatest velocity relatively to the corpuscles, and therefore would, other circumstances being the same, be the least likely to capture them. The heavier the particle, the slower is its velocity, and the greater chance it has of capturing the corpuscles; the fact that heavy complicated particles are conspicuous by their absence on the negative side, shows that the attraction of these for the corpuscles must be exceedingly small compared with that exerted by a neutral atom of hydrogen. It will be seen that the atom of carbon, also regarded as an electro-positive element, is also conspicuous on the negative side.

On looking at the list of the particles which occur on the negative side, we are struck by the fact that they are all atoms; there is not a molecule among them. Thus, although the curve corresponding to the negatively electrified hydrogen atom occurs on every plate, there is not a single plate which shows a trace of a curve corresponding to a negatively electrified hydrogen molecule, although that corresponding to the positively electrified molecule is always present, and on some of the plates is stronger than that due to the positive hydrogen atom. Again, on some plates the positive oxygen molecule shows stronger than the oxygen atom, but on the negative side only the atom is visible.

Thus neutral atoms, but not neutral molecules, can exert on the negative corpuscles those enormous attractions which, under the conditions of these experiments, are required to bind the corpuscles to these rapidly moving particles. We may compare this result with the properties ascribed by chemists to bodies when in the nascent condition; *i.e.*, when they have only recently been liberated from chemical combination, and when they are likely to be partly in the atomic state; for atoms, as we have seen, exert forces on electric charges in their neighbourhood vastly greater than those exerted by molecules.

We may compare the forces exerted by a neutral atom on the corpuscles with those exerted by an unelectrified piece of metal on a charged body in its neighbourhood. In consequence of electrostatic induction, the charge and the metal will attract each other. This attraction is dependent on the electricity in the metal being able to move under the electric forces exerted by the charge, and to re-arrange itself in such a way that if the charge is positive, the negative electricity in the metal moves to the part of the metal nearest to the charge, while the positive electricity moves to the part remote from the charge. The force between the metal and the charge depends on the freedom of the electricity to move about in the metal under the action of the electric field. If the metal is replaced by a substance of high specific inductive capacity, like sulphur, in which the electricity has an appreciable amount of freedom, though not so great as in a metal, the attraction, though still appreciable, is very much less than it was with the metal. A very simple experiment will illustrate this point. I have on this cardboard disk, which is suspended from a long string, a number of magnets, such as are used for compasses; if I mount the magnets on pivots, so that they are free to turn round, the system of magnets is strongly attracted when another magnet is brought near it; if, however, I take the magnets off their pivots so that they are no longer free to turn, the magnet exerts very little attraction upon them.

A view of chemical combination which I gave some time ago in the *Philosophical Magazine*, and also in my "Corpuscular Theory of Matter," suggests that there is a very close analogy between the causes at work in the experiment we have just made and those which produce the difference between the behaviour of atoms and molecules. On that theory the atom was supposed to consist of a large number of corpuscles arranged inside a sphere of positive electricity; the corpuscles arranging themselves so as to be in equilibrium under their mutual repulsion and the attraction of the positive electricity. The configuration depends on the number of corpuscles, and the stiffness and stability of the system also change as the number changes. For some particular numbers of corpuscles the system is very rigid, and any movement of the corpuscles would be strongly resisted; since the movement of electricity inside the atom is brought about by the movement of the corpuscles, the electricity could only move with great difficulty inside these atoms, and they would therefore not be able to exert more than feeble forces on electrical charges outside the atom; they would therefore not enter readily into combination with other atoms. We may ascribe such a constitution as this to the atoms of the inert gases, helium, argon, and neon. A system with one, two, or three more corpuscles than the system we have just described would not be nearly so stable, and there would be a tendency to discard the extra corpuscles from the atom so that it might return to the more stable form. We may roughly picture to ourselves the atom with one extra corpuscle as consisting of a number of fixed corpuscles plus one which is free to move about; the freedom of this corpuscle would enable the electricity in the atom to move about, and would endow the atom with the property of attracting any electrical charges which might be near it. If there were two corpuscles in the atom more than the number required for the most stable form, we can picture the atom as having two corpuscles free and the rest fixed. Similarly, if we had more than two extra corpuscles. Thus we may regard the atom as possessing 0, 1, 2, 3 corpuscles which are able to move about with more or less facility, and the free corpuscles will give to the atom the power of exerting attractions on electrical charges to an extent which depends on both the number of corpuscles and the freedom with which they can move about. On the theory to which I have alluded the number of these "free" corpuscles determines the valency of the atom.

Now, let us suppose that two such atoms come into such close connection that the corpuscles in the one exert considerable forces on those in the other. The system consisting of the two atoms will rearrange itself so as to get into a more stable form, if necessary corpuscles passing from one atom to the other to enable it to do so. The greater stability, however, implies a loss of mobility; the free corpuscles have become parts of a more stable system, and have therefore lost to a greater or less extent their mobility. But with the mobility of the corpuscles goes

their power of exerting forces on electrical charges; and thus the combination of the atoms diminishes to a great extent the attractions they exert outside them. Speaking generally, we may say that on this view the combination of atoms to form molecules, either of compounds or elements, fixes corpuscles which were previously mobile and converts the atoms from conductors of electricity into insulators with a small specific induction capacity.

I have brought these illustrations before you with the object of showing that we have now methods which are capable of dealing with much smaller quantities of matter than the methods now used by chemists, methods which are capable of detecting transient phases in the processes of chemical combination, and I am hopeful may be of service in throwing light on one of the most interesting and mysterious problems in either physics or chemistry—the nature of chemical combination.

ORGANIC AMALGAMS: SUBSTANCES WITH METALLIC PROPERTIES COMPOSED IN PART OF NON-METALLIC ELEMENTS.*

By HERBERT N. McCOY and WILLIAM C. MOORE.

(Continued from p. 259).

D. *The Electrode Potential of the Electrode; Tetramethyl Ammonium Amalgam, Half-normal Tetramethyl Ammonium Chloride in Absolute Alcohol, and in Water.*

THE electromotive force of the electrode, tetramethyl ammonium amalgam, 0·5 N $N(CH_3)_4Cl$ in absolute alcohol, was measured, at 0°, against a decinormal calomel electrode. Measurements were made by a compensation method and were carried out both while the primary or polarising current was running and after the amalgam had been formed and the polarising current was cut off.

In order to make the measurements while the polarising current was running, it was necessary very rapidly to shift the connections of the amalgam electrode from the polarising circuit on the one hand to the measuring circuit on the other. Le Blanc (*loc. cit.*) used for this purpose an electric tuning-fork, but in the present work a re-modelled electric bell gave better results as a vibrator. The gong and clapper were removed, and a platinum contact point passed through the clapper stem, so that when the armature of the bell was in motion it made contacts in such a way that the amalgam electrode was alternately in connection with the polarising circuit and the measuring circuit. When the vibrator was at rest, permanent connection was made between the amalgam electrode and the measuring circuit.

Since the electrode potential of the amalgam was measured against a decinormal calomel electrode, both while the polarising current was running and after it was cut off, provision had to be made for the anode of the polarising circuit. This anode was made of silver wire, and was run between the stopper and the edge of the glass half-cell serving as container for the mercury forming the cathode. Connection between this mercury and the negative terminal of the polarising circuit (through the circuit shifter) was made by means of a platinum wire sealed into a glass capillary filled with mercury. This capillary passed through a hole in the rubber stopper. The glass half-cells containing the amalgam and calomel electrodes were immersed in crushed ice, while the capillary portions of the cells extended over the edge of the ice-bath into the "bridge" solution of decinormal potassium chloride. The mercury used in the preparation of the decinormal calomel electrode, and as a cathode in the amalgam cell, was recently purified by distillation in a vacuum. A D'Arsonval galvanometer was used in the measuring circuit. In all instances the "zero" method of measurement was used.

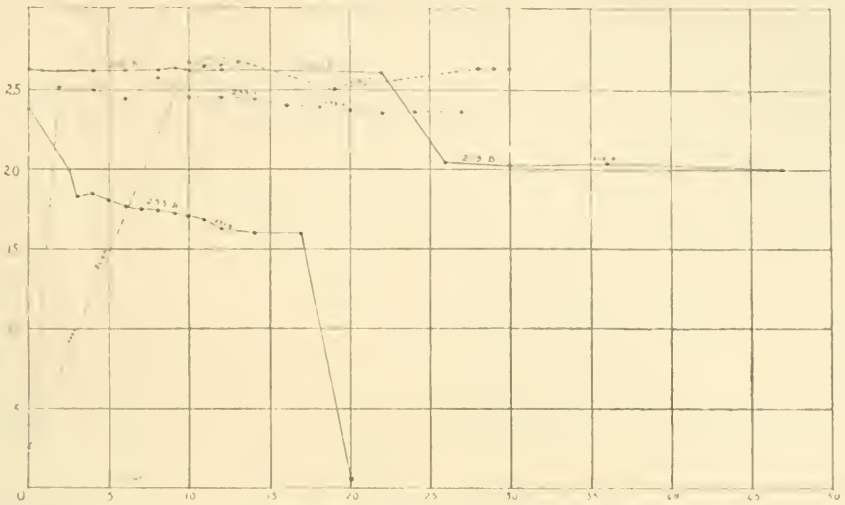
The compensating current in the measuring circuit was derived from two storage cells; the polarising current was taken from the lighting circuit of the laboratory, and by means of a variable resistance in parallel with the electrolytic apparatus the voltage was regulated without difficulty.

TABLE III.—*Electromotive Force of the Amalgam-Calomel Electrode Cell at 0°.*

Expt. No.:	205.	206.	209.
Time (mins).	E.M.F. (volts).	E.M.F. (volts).	E.M.F. (volts).
	A. *Polarising Current on.*		
0	0·229	0·240	0·247
8	—	2·928	—
10	—	2·908	2·681
11	—	—	2·664
12	2·807	2·908	2·664
13	—	—	2·681
14	—	2·97	—
15	2·807	—	—
16	—	2·96	—
18	2·626	—	—
19	—	3·034	2·502
21	2·611	—	—
22	—	3·034	—
24	2·611	—	—
25	—	2·990	—
27	2·611	2·990	—
28	—	—	2·630
29	—	—	2·630
30	—	—	2·630
	B. *Polarising Current off.*		
0	2·6111	2·990	2·630
1·5	2·628	—	2·622
2	—	2·671	2·618
4	2·629	2·648	2·618
6	2·628	2·621	2·618
8	—	2·605	2·617
9	2·624	—	2·622
10	—	—	2·617
12	—	1·984	2·617
14	—	1·948	—
15	—	—	2·615
19	—	1·062	—
20	2·017	—	—
22	—	—	2·604
25	1·958	0·477	—
26	—	—	2·041
30	—	—	2·031
36	—	—	2·031
37	0·503	—	—
47	—	—	2·001

In making a measurement the electromotive force of the two storage cells was first balanced against that of a cadmium cell. The polarising current was then allowed to flow continuously through the half-cell in which the amalgam was to be formed for several minutes. The connections having in the meanwhile been changed from the cadmium cell to the amalgam calomel electrode cell, the electric vibrator was set in motion, and the e.m.f. of the cell: Amalgam, 0·5 N $N(CH_3)_4Cl$ in absolute alcohol, 0·1 N KCl, 0·1 N calomel electrode, balanced against that of the two storage cells at intervals. After making measurements in this way for some minutes, the primary or polarising circuit was broken, and the e.m.f. of the cell again measured at intervals. After completing this set of measurements the current of the storage cells was again balanced against that of the cadmium element, and the average of the two values of the electromotive force of the

* Preliminary report read at the Detroit Meeting of the American Chemical Society, June, 1909 (*Science*, 1909, xxx., 315). From the *Journal of the American Chemical Society*, xxxiii., No. 3.



Electrode Potentials of Tetramethyl Ammonium Amalgam Measured against a Decinormal Calomel Electrode at 0° C.

Electrolyte in 209, N/2 $N(CH_3)_4Cl$ in absolute alcohol. Electrolyte in 233, N/2 $N(CH_3)_4Cl$ in water.

storage cells used in calculating the electromotive force of the amalgam calomel electrode cell. These two values of the electromotive force of the storage cell were always close together. The detailed results of these experiments are given in Table III.

In the series of values given when the polarising current was cut off the value for zero time is taken as the same as the final value obtained just before the polarising current was cut off.

In addition to the potential measurements above, the potential of an amalgam cell, using water as the solvent, for tetramethyl ammonium chloride, of half-normal concentration, was determined. This set of measurements was likewise made against a decinormal calomel electrode, at zero, in a manner exactly similar to that above. The results of this experiment, with the polarising current on (Series A) and off (Series B), are given in Table IV.

The curves for two experiments, Nos. 209 and 233, the one in which alcohol was the solvent, and the other, in which water was the solvent, are shown in Fig. 1.

(To be continued).

Table IV.

Time (mins.).	Series A.
0	0·219
2	2·507
2·5	—
4	2·507
6	2·452
8	2·571
10	2·46
12	2·46
14	2·448
16	2·387
18	2·387
20	2·373
22	2·352
24—27	2·359

Time (mins).	Series B.
0	2·359
2·5	1·99
3	1·831
4	1·844
5	1·811
6	1·763
7	1·752
8	1·736
9	1·714
10	1·699
11	1·678
12	1·637
14	1·596
17	1·591
19	0·063

CHEMICAL ENGINEERING EXHIBITION.

Exhibitors' Dinner.

To celebrate the successful results of the above Exhibition, which has been held during the last fortnight at the Agricultural Hall, an Exhibitors' Dinner took place on Monday, May 29th, at the Holborn Restaurant, when a fair number attended under the chairmanship of Mr. Edmund White, now of 2, St. Dunstan's Hill, E.C., late of Alfred White and Sons.

After the toast of the King had been proposed by the Chairman, Mr. G. A. Mercer proposed "The Exhibition." He said that the Exhibition had successfully achieved its purpose of bringing more closely together the chemical engineer and the chemical expert to their mutual advantage by the interchange of ideas, and had attracted those who had a practical interest in the Exhibition. They all owed a debt of gratitude to Mr. Walter Reid, Mr. Bridges, and Prof. Meldola, without whose valuable assistance the Exhibition could not have been brought to such a successful issue.

He wished also to pay tribute to the Right Hon. The Earl of Denbigh, who opened the Exhibition, and who contributed a valuable paper on "Beetroot Sugar"; also to the other contributors of valuable papers.

In support, Mr. W. A. Davis, while regretting the paucity of exhibitors and in particular the absence of chemical manufacturers, hoped that this would be remedied on the next occasion, and was sure that great benefit had accrued to such as were present. He hoped that they had seen but the first of a series of such exhibitions, and expressed his personal satisfaction with the results.

Mr. F. W. BRIDGES, in reply, said that he felt somewhat diffident as he was only one of several who had promoted the success of the Exhibition. However, he had stood the financial part, and as he would have been the one to be shot at in case of failure, so he felt the honour of success. He had never had any doubt as to the ultimate success of the Exhibition. Some of the exhibitors originally took space in the Engineering Exhibition; at a later date it was decided to give chemical engineering a wider scope, and to take the Agricultural Hall. There were certain gentlemen who thought they were too previous, and doubted the need for such an exhibition; but there always were people afraid of a new venture until it was well on its way to success. While he appreciated "sitting on the fence" he liked those who took their courage in their hands and did what they said they would do. It would be a white lie to say that he was completely satisfied, but he was not discouraged, and while he did not think he would be justified in advising another exhibition next year, he would be quite willing to undertake the organising of one in two years' time. In conclusion he thanked the exhibitors for their support.

Mr. H. C. BATCHELOR proposed "Our Guests," and Prof. MELDOLA, Mr. WALTER REID, and Mr. T. TYRER responded

"The Chairman" was proposed by Mr. BOOTH, who stated that it was due to Mr. White that the dinner had been such a success, thanks to his energy in the short time that had elapsed between its proposal and its taking place.

Mr. WHITE, in responding to the toast, said he had been brought up practically from his cradle in chemistry and engineering; his father being connected with one of the oldest chemical manufacturing businesses in London, and having been apprenticed in his early days to a firm of engineers, and being afterwards at Palmers, of Jarrow, could therefore say from experience how important it was to have a knowledge of those two great professions. He was most delighted to be connected with the First International Chemical Engineering Exhibition, for he felt sure that it was only the first of many others.

The Chairman also called upon Dr. Walmsley and Mr. Newlands to say a few words during the evening.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 25th, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Experiments on the Compression of Liquids at High Pressures.*" By the Hon. C. A. PARSONS, F.R.S., and S. S. COOK.

During the experiments on the behaviour of carbon under high pressures and temperatures described in a paper by Mrs. C. A. Parsons, June 27, 1907, to the Royal Society, very considerable volumetric compressions were observed in the case of oils and other liquids. The present paper records some investigations into those compressibilities.

The apparatus consists of a hydraulic press capable of exerting a maximum force of 2000 tons. Under the press is placed a massive block of gun steel, with a 4-inch hole and plunger of tool steel packed with a cup leather reinforced by a brass cup, which has been found to be satisfactory up to pressures of 40 tons per square inch, and quite tight for fluids. The estimation of the total friction by the method of the loop diagram, and the correction for the elasticity of the mould packings and ram by the method of replacing a known volume of the fluid by steel, are fully described, and the pressure in the mould is given by the water gauge pressure on the rams of the press, plus the weight of the moving parts multiplied by the constants.

The fall of temperature on sudden removal of pressure and the curves for isothermal and adiabatic compression are given for some fluids. From these data the internal work of the fluid is calculated for water, ether, and paraffin oil.

In the preliminary experiments the pressure was carried up to 40 tons per square inch, but because no advantage was apparent and some inconvenience was involved, the pressure was limited to 4550 atmospheres, under which water is compressed to 87 per cent of original bulk.

The results as to compressibility are in close agreement with those of Amagat as far as the latter were carried, *i.e.*, 3000 atmospheres.

"*Energy Transformations of X-rays.*" By Prof. W. H. BRAGG, F.R.S., and H. L. PORTER.

There seems to be good reason to suppose that the energy of the secondary cathode-ray comes from the energy of the primary X-ray. This leads to the "corpuscular" theory of the X-ray (and similarly of the γ-ray). Each such ray must move without gradual change of form or energy until at last an atom through which it is passing causes the conversion of form, that is to say, the transformation to cathode-ray energy.

On this view (1) the absorption of X-rays means simply the transformation of energy, and (2) the X-ray itself does not ionise at all.

The present paper describes experiments intended to test these deductions. The results show that in the cases considered the second deduction is verified, and the first also, when the test can be pushed to completeness. In some cases insufficient knowledge of the law of absorption of the cathode-rays, and of other important processes, prevent the full application of the test, but it is satisfactory as far as it goes.

"*Spectroscopic Investigations in Connection with the Active Modification of Nitrogen. I. Spectrum of the Afterglow.*" By Prof. A. FOWLER, F.R.S., and the Hon. R. J. STRUTT, M.A., F.R.S.

1. The paper gives a detailed account of the spectrum of the afterglow of pure nitrogen, with wave-length determinations of sufficient accuracy to indicate the series relationships of the various bands.

2. The characteristic bands of the afterglow in the red, yellow, and green are complex groups which have been found to be identical with some of the bands forming the sequence known as the first positive group of nitrogen. They represent a special development of three of the numerous series into which the first positive bands have been divided.

3. The second group of afterglow bands, extending from 4312 to 2503, corresponds with a group of faint bands which occur in the uncondensed discharge in air or nitrogen, and the third group is identical with the third positive group of nitrogen bands, as previously shown by Lewis.

4. The most characteristic feature of the condensed discharge which produces the afterglow is a series of seven complex bands, occupying the region 2904 to 2256, which have not previously been recorded as belonging to nitrogen. It is suggested that these should be designated the "fourth positive" group of nitrogen bands.

5. No afterglow is excited when the discharge is such as to give only the line spectrum of nitrogen.

"*An Optical Method of Measuring Vapour Pressures: Vapour Pressure and Apparent Superheating of Solid Bromine.*" By C. CUTHBERTSON and Mrs. M. CUTHBERTSON.

The vapour pressures of solid bromine between $-80°$ C. and the melting-point have been measured by counting the number of interference bands which pass across the field of a Jamin refractometer as the temperature of the solid is gradually raised. The vapour pressure curve ob-

tained agrees well with that observed by Ramsay and Young down to -17° C.

The behaviour of the vapour pressure near the melting-point is remarkable, and suggests the inference that superheating of the solid occurs.

"*Vacuum Tube Spectra of Mercury.*" By Frank Horton, D.Sc., M.A., St. John's College, Cambridge.

Under certain conditions mercury vapour may be made to give several different line spectra in which the number of lines appearing ranges from 5 in the simplest case (the yellows 5791, 5770, the green 5461, the blue 4916, and the violet 4359) to a very large number in the case of the "many-lined spectrum" first observed by Eder and Valenta. The observations were made directly by means of a direct wave-length reading spectroscope, and several new bright lines are recorded in the red and orange regions of the spectrum. The luminosity was excited in three different ways—

1. By means of the discharge from a glowing line cathode;
2. By an induction coil discharge through the vapour at different pressures, and with different amounts of capacity in the circuit;
3. By means of the electrodeless ring discharge.

Five distinct spectra were recognised, all of which may be obtained with the induction coil discharge by suitably regulating the conditions. The glowing lime discharge gives one of the simplest spectra; the electrodeless ring discharge gives the spectrum containing most lines.

"*Production of Characteristic Röntgen Radiations.*" By R. Whiddington, B.A.

A characteristic radiation can usually only be excited when the velocity of the cathode rays within the X-ray tube supplying the primary rays exceeds a certain value depending on the radiator. The value of this critical speed v_c has been accurately determined for the radiators Cr, Fe, Ni, Cu, Zn, Se; that for Al has been given in a previous paper.

It appears that for the radiators studied v_c is proportional to the atomic weight of the emitting element being very nearly 10^8 times the atomic weight. The potentials corresponding to these velocities range between 7320 volts and 15,400 volts.

An interesting result obtained during the course of the investigation is that the energy emitted in the form of Röntgen radiation by a cathode particle when suddenly stopped is proportional to the fourth power of its velocity.

CHEMICAL SOCIETY.

Ordinary Meeting, May 18th, 1911.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

Messrs. E. E. Walker, C. H. Hampshire, H. Christopher, H. F. Harwood, and Noel Deer were formally admitted Fellows of the Society.

The President announced that a number of valuable chemical works of much historical interest had been presented to the Society by the family of the late Dr. W. J. Russell, F.R.S.; among them was a rare edition of Basil Valentine's "Triumphant Car of Antimony," bearing an earlier date than the copy in the British Museum.

The Council, at its meeting that afternoon, had passed the following resolution:—

"That the best thanks of the Council be accorded to the family of the late Dr. W. J. Russell, F.R.S., for their generous bequest of a number of chemical works of historical interest."

The President reminded the Fellows that Prof. Theodore W. Richards would deliver the Faraday Lecture, entitled, "The Fundamental Properties of the Elements," in the Theatre of the Royal Institution, on Wednesday, June 14th, 1911, at 8 p.m.

Certificates were read for the first time in favour of Messrs. Norman Ernest Atkinson, Ash Cottage, Thornhill Lees, Dewsbury; Thomas Cowling, Easingwold, Yorks; Rudolph Demuth, 68, Salusbury Road, N.W.; Cyril Herbert Koszelski Gonville, Milton, Queen's Road, Buckhurst Hill; Henry Edmund Linenbroker, 100, Harrow Road, Paddington, W.; Leonard Ison Pitt, B.Sc., 109, Abbott Road, Bromley, E.

A Certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Benjamin Gallsworthy, Thilawa, Burma.

International Association of Chemical Societies.

At a conference of delegates from the English, French, and German Chemical Societies, held in Paris on April 25th and 26th, it was decided to form an International Association of Chemical Societies. The delegates appointed by the three Societies were:—

The Chemical Society, London—Profs. Percy Frankland, Meldola, and Sir William Ramsay.
Société Chimique de France—Profs. Béhal and Haller, and M. Hanriot.
Deutsche Chemische Gesellschaft—Profs. Jacobson, Ostwald, and Wichelhaus.

The following Statutes of the Association, drafted by the delegates at the Paris conference, were approved by the Council of the Chemical Society at their meeting on May 18th.

Statutes.

Art. 1. Il est fondé une Association internationale des Sociétés chimiques.

Art. 2. Le but de l'Association est de former un lien entre les Sociétés chimiques du monde, pour s'occuper des questions ayant un intérêt général et international pour la Chimie.

Art. 3. Toutes les Sociétés chimiques peuvent faire partie de l'Association.

Art. 4. L'Association est dirigée par un Conseil formé d'un certain nombre de membres. Chaque pays ne peut être représenté dans le Conseil que par une seule Société chimique, qui désignera trois représentants.

Art. 5. Le Conseil actuel comprend les délégués des Sociétés fondatrices, c'est-à-dire de la Société chimique allemande (Deutsche chemische Gesellschaft), de la Société chimique anglaise (The Chemical Society, London) et de la Société chimique française (Société chimique de France).

La représentation d'une autre Société dans le Conseil ne pourra etre décidée que par celui-ci, et à la majorité des deux tiers des votants. Le vote par correspondance sera admis dans ce cas.

Art. 6. Le Conseil fixe à chaque réunion le lieu et l'époque de la prochaine session.

Art. 7. Le Conseil nomme au début de chaque session un Président, qui est en même temps Président de l'Association, et qui entrera en fonctions à la fin de la Session.

Art. 8. Le Bureau est constitué par le Président, le Vice-Président et le Secrétaire Général qui sont les délégués du même pays.

Art. 9. Le Président est chargé de convoquer le Bureau. Celui-ci veille à l'exécution des décisions prises par le Conseil: il fixe l'ordre du jour des Séances du Conseil et entretient des relations entre les diverses Sociétés. Le Président fait approuver les procès-verbaux des séances. Seul le procès-verbal de la dernière séance peut être approuvé par correspondance.

Art. 10. Les moyens d'action de l'Association consistent:—

En nomination de Commissions chargées d'étudier les questions qui leur seront soumises par le Conseil;

En publication dans les journaux des Sociétés affiliées ou en tout autre mode de publication qu'il conviendra au Conseil de choisir ;

En Conférences et Congrès.

Art. 11°. Les frais généraux seront supportés par les Sociétés affiliées au prorata du nombre de leurs membres.

(NOTE.—L'article 11 ne deviendra définitif qu'après l'acceptation des trois Sociétés foundatrices.

Toutes les dépenses autres que les frais généraux ne seront imputables aux diverses Sociétés que sous réserve d'un engagement personnel de ces Sociétés.

Le Secrétaire Général soumettra à chaque session à l'approbation du Conseil le compte-rendu financier de l'exercise écoulé.

Art. 12. Les modifications aux présents statuts ne pourront être votées qu'à la majorité des deux tiers des membres du Conseil. Le vote par correspondance est encore admis dans ce cas.

The Association proposes, in the first instance, to appoint international committees to consider and report on the following questions:—

Nomenclature of Mineral Chemistry ;
Nomenclature of Organic Chemistry;
Unification of the Modes of stating Physical Constants.

Prof. Ostwald has been elected President of the Association for the ensuing year, and the next meeting has been fixed for April 13th, 1912, and is to take place in Berlin. The meeting in 1913 will be held in Great Britain.

Of the following papers those marked * were read :—

*134. "*Some Reactions of ω-Bromomethylfurfuralde hyde.*" By WILLIAM FRANCIS COOPER and WALTER HAROLD NUTTALL.

ω-*iso*Cyano- or ω-cyano-methylfurfuraldehyde cannot be prepared by the action of potassium or silver cyanide on ω-bromomethylfurfuraldehyde in alcoholic solution ; owing to the great re-activity of the bromine atom in the ω-position, condensation of the furfuraldehyde with the alcohol takes place, with the production of ω-ethoxymethylfurfuraldehyde and the liberation of hydrogen bromide. The latter reacts with the silver cyanide, and hydrogen cyanide is evolved.

The same ethoxy-aldehyde may also be prepared by boiling an alcoholic solution of ω-bromomethylfurfuraldehyde with excess of calcium carbonate to neutralise the liberated hydrogen bromide.

ω-*Ethoxymethylfurfuraldehyde* is a yellow oil, readily soluble in the usual organic solvents ; it dissolves in hot light petroleum, but is insoluble in the cold. It is also moderately soluble in water. When rapidly distilled, it boils at 235 - 240° without decomposition, but prolonged heating induces polymerisation. Under 35 mm. pressure it boils at 145°, and it has D 15·5/15·5 1·1096. It shows all the usual properties of a furfuraldehyde.

The *phenylhydrazone* forms long slender yellow needles, melting at 55·5—56·2°, and the p-*bromophenylhydrazone* crystallises in shining silky needles, melting at 104 - 105°.

ω-*Ethoxymethylpyromucic acid* is prepared by oxidising the above aldehyde with silver oxide. It is soluble in water, alcohol, ether, benzene, chloroform, or carbon disulphide, but insoluble in light petroleum, and forms long colourless needles, melting at 57·5—58·5°.

ω-*Methoxymethylpyromucic acid* is obtained by oxidising ω-*methoxymethylfurfuraldehyde* prepared from ω-bromomethylfurfuraldehyde and methyl alcohol. It crystallises in long silky needles, melting at 67·5—68·5°.

ω-Methoxymethylfurfuraldehyde, on oxidation with alkaline permanganate, gives dehydromucic acid. When ω-bromomethylfurfuraldehyde is boiled with water in the presence of barium carbonate, it gives ω-hydroxymethylfurfuraldehyde ; under certain conditions, however, a beautiful yellow crystalline *compound*, $C_{11}H_{10}O_4$, is obtained, which melts at 111·5—112°. The compound may possibly be a condensation product of ω-bromomethylfurfuraldehyde and lævulic acid, the latter being formed by the decomposition of ω-hydroxymethylfurfuraldehyde: $C_6H_5O_2Br + C_5H_8O_3 = C_{11}H_{10}O_4 + HBr + H_2O$.

DISCUSSION.

Dr. PYMAN pointed out that the conversion of ω-bromomethylfurfuraldehyde into ethoxymethylfurfuraldehyde by means of alcoholic potassium cyanide was analogous to the conversion of 4(or 5)-chloromethylgloxaline into ethoxymethylglyoxaline under similar conditions (*Trans.*, 1911, xcix., 678). 4(or 5)-Chloromethylglyoxaline hydrochloride could, however, readily be converted into 4(or 5)-cyanomethylglyoxaline by adding its absolute alcoholic solution to ice-cold saturated aqueous potassium cyanide.

Mr. CROSS suggested that the analogous reaction with alcoholic hydroxyl groups of cellulose might explain the limit of resolution of cellulose to ω-bromomethylfurfuraldehyde (Fenton).

Mr. NUTTALL, in reply, said that the authors did not claim that the reaction of ω-bromomethylfurfuraldehyde with potassium or silver cyanide was unique, but merely unusual. A 30—40 per cent yield of ω-bromomethylfurfuraldehyde could be obtained from cellulose by heating with hydrobromic acid in chloroform solution under pressure at 100°. In addition, a considerable quantity of insoluble "humus" was formed, and for some time the authors had been making an exhaustive examination of this product, and had obtained some interesting acids by oxidation.

*135. "*A Method for the Accurate Volumetric Deter mination of the Oxygen in Air.*" By HERBERT EDMESTON WATSON.

An apparatus was described in which about 50 cc. of air are first measured at constant volume. The gas is then passed into a vessel containing phosphorus, which is warmed, and the residual gas finally re-introduced into the measuring vessel without removal from the apparatus. The accuracy of the method was discussed, and some preliminary results were given. These show that different analyses of the same sample usually agree to 2 parts in 10,000. A complete analysis can readily be performed in an hour and a-half.

DISCUSSION.

Dr. WADE thought that the relative increase in accuracy above that obtainable with Haldane's well-known compensator burette was not commensurate with the comparatively large increase in complexity and in the time required. In his experience the percentage of oxygen in air could be determined by the compensator method with an accuracy of ± 1 part per 1000.

Mr. WATSON, in reply to the President, said that Regnault's method of air analysis was objectionable because it involved the use of moist gases, and for accurate work a compressibility correction had to be applied. Ammonia was also formed by the explosion of air and hydrogen, thereby vitiating the absolute results. Regnault's absolute values were slightly lower than those found with the present apparatus, which agreed with those of Leduc.

*136. "*Mannitoboric Acid.*" By JOHN JACOB FOX and ARTHUR JOSIAH HOFFMEISTER GAUGE.

Mannitoboric acid, $C_6H_{15}O_8B$, is prepared from mixtures of mannitol and boric acid dissolved in absolute alcohol. It separates from the alcoholic solutions in tufts of prisms, melting at 89·5°. The acid dissolves readily in water or hot alcohol, but is decomposed by these solvents. Mannitoboric acid behaves as a monobasic acid, and yields normal *ammonium*, *silver*, *calcium*, and *barium* salts. The salts are crystalline powders, soluble in water, and precipitated from aqueous solutions by alcohol.

Measurements of the rotations of mixtures of mannitol and boric acid were made, both in alcohol and in water. The results indicate that the formation of mannitoboric acid is favoured by increasing the concentration of either the mannitol or the boric acid.

Discussion.

Dr. Fox, in reply to the President, stated that the curves for the rotation of mixtures of mannitol and boric acid in alcoholic solutions appeared to reach a maximum; the fact that it was impossible to dissolve larger quantities of boric acid than those used had prevented the authors from following the curves to their completion. In one or two cases, however, a maximum value had been obtained.

(To be continued).

PHYSICAL SOCIETY.

May 26th, 1911.

Visit to the National Physical Laboratory.

All departments of the Laboratory were thrown open for inspection, and, in addition, a number of special demonstrations had been arranged.

Mr. G. S. Baker described the apparatus which has been installed for the moulding and shaping of ship models in connection with the work of the National Experimental Tank.

The models are made of paraffin wax. The wax is heated in a tank surrounded by hot water which is kept circulating by a small boiler. The castings are made in a clay mould, the tank containing the clay being arranged so that two moulds for 20 ft. models may be prepared at the same time. A travelling cutter is provided on the top of the mould tank for trimming the upper surface of the castings.

The models are shaped to the correct form by cutting a series of horizontal grooves in them on a special machine, and trimming the wax down by hand to a fair and smooth surface, leaving only the finest traces of these grooves. The shaping machine will deal with models of a maximum length of 25 ft.

A table for measuring the finished model or marking any desired lines on the model has been installed.

The Silica Standard Metre Bar, recently constructed as a primary standard of length, was shown by Mr. J. E. Sears and Dr. Kaye.

The remarkably low coefficient of expansion of fused silica, and its practical freedom from thermal hysteresis, render it a specially suitable material for the construction of permanent length standards of the highest class. Such standards are always handled by trained and skilled observers, so that its comparative fragility is of small import. It is only recently, however, that sufficient progress has been made in methods of manufacture to render possible the construction of a length standard in silica. The present bar, which is the first of its kind, consists of a silica tube into which are fused at its two ends optically worked plane parallel slabs of silica which carry the graduations. The undersides of these slabs are platinised, and the graduations made by cutting through the platinum film with a diamond point. The rulings are viewed from above through the thickness of the silica end-slabs, so avoiding any apparent alteration of length which might be caused by the shifting of the cover slips which are used to protect the platinum film. The bar is supported at two points, one of which is defined by a trunnion of silica fused into the tube, and the other by a ring etched round it. In this way the conditions of support can be exactly reproduced whenever the bar is under examination. The thickness and position of the end slabs are so arranged that the apparent image of the ruling, when the bar is immersed in water, lies in the neutral axis.

Mr. C. G. Eden gave a demonstration of apparatus for the visual and photographic study of the flow past plates and models in a slow stream of water.

The eddies from a square plate inclined 45° to the stream were made visible by means of a filament of red ink which is introduced into the stream above the plate.

The eddies are periodic, and are similar in structure to vortex rings.

The nature of the flow past model dirigibles can be shown by the same method.

Dr. W. Rosenhain and Mr. J. C. W. Humfrey demonstrated their apparatus for making Delicate Tensile Tests on strips of steel at high temperatures *in vacuo*.

One end of the specimen is attached to a cast-iron float carried by mercury, and stress is applied by admitting mercury to the float chamber; the level of the mercury and the movement (rise) of the float are used to give an autographic stress-strain diagram. The specimen is hung inside a vertical porcelain tube which moves with the float: the lower end of this tube dips in mercury, and the interior of the tube is exhausted by powerful pumps. A small electric resistance furnace heats that part of the tube which contains the specimen. The specimens are polished for microscopic examination before they are tested, and remain perfectly bright at the highest temperatures, thus allowing the nature of the slip-bands to be observed. Results obtained with the apparatus show marked changes in the properties of pure iron associated with the allotropic transformations.

Mr. F. E. Smith gave a description of the Lorenz apparatus presented by the Drapers' Company, in memory of the late Prof. J. Viriamu Jones, F.R.S.

The apparatus was designed at the National Physical Laboratory, and constructed at Elswick by the kindness of Sir Andrew Noble. It is intended for the direct measurement of resistances of 0·002 ohm, of 0·01 ohm, and of 0·1 ohm. For these measurements the discs revolve at about 1044 revolutions per minute, and a directly driven chronograph enables the speed to be estimated within 1 part in 100,000. The object of having two discs is to make the apparatus astatic with respect to the earth's field, and to place in opposition the thermal E.M.F. produced at the points of contact of brushes and disc. It is not necessary to know the circumference of a disc with great accuracy, as the circumference is in zero magnetic field. With the exception of the motor, the apparatus is free from any magnetic substance. The effect of the motor on the mutual induction of two coils and a disc is very small, and can be compensated. The lubrication is forced, at a pressure of about 10 lb. per square inch; 1 cubic ft. of oil passes through the bearings every five minutes.

In the Photometric Division Mr. C. C. Paterson and Mr. B. P. Dudding explained some experimental work now in progress in connection with the visibility of ships' lights, and particularly that of the green starboard lanthorns carried by all sea-going craft.

The apparatus shown in the laboratory was in the nature of a portable and variable standard of visibility against which the visibility of any distant point source of light could be measured. The unit of visibility of a point source was taken as the millionth part of a candle at a distance of 1 metre.

This amount of light could readily be seen, and point sources only begin to vanish for persons of ordinary vision when their visibility is of the order of one or two ten-millionths of a candle metre.

Laboratory experiments on the principles underlying visibility were made possible by substituting for the distant light an illuminated pinhole. A series of such pinholes had been made varying from 0·2 mm. to 0·01 mm., and observations conducted in the laboratory up to distances of 150 metres by different observers.

In the Electrical Division Mr. Campbell and Mr. Dye showed on a screen Spark Trains in which the separate oscillations were visible up to about 1,000,000 vibrations per second. The image was thrown on a screen by a concave mirror (at a distance of 2 metres), rotating

speed of 50 to 100 revolutions per second. A demonstration was also given of Carey Foster's method of testing condensers from 1 micro-mfd. up to 1 mfd.

Mr. E. H. RAYNER demonstrated the use of small three-legged Tilting Tables with Mirrors as applied to the measurement of thin plates, giving a magnification of 4000. An application of this was shown to the measurement of the bending of a cantilever consisting of a horizontal brass rod 200 metres long by 3 mm. diameter. By calibrating the scale with known weights a spring balance is made to give 1 metre deflection for 50 grms.

By fixing to a tilting table a horizontal rod to the end of which the moving point of a second tilting table is suspended, a great increase in sensitiveness may be obtained. An arrangement magnifying 400,000 times was shown for the demonstration of the changes in length of a short iron bar when magnetised.

A calibrating lever for the accurate determination of the "working distance" of three-legged tables was also shown.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 31st, 1911.

Mr. E. W. VOELCKER, President, in the Chair.

MR. Alfred Douglas Heywood was elected a member of the Society.

Certificates were read for the first time in favour of Messrs. Ronald Devereux Carty, The Laboratories, Survey Department, Public Works Ministry Gardens, Cairo; George Frederick Wesley Martin, Castle Park, Lancaster; and William Keighley Walton "Beechwood," Upper Rushton Road, Thornbury, Bradford.

A certificate was read for the second time in favour of Mr. Horace C. Huish.

The following papers were read and discussed :—

"*The Composition of Milk*," By H. DROOP RICHMOND.

The author gives an abstract of the results of analyses of milk made in the laboratory of the Aylesbury Dairy Company during 1910.

"*Notes on the Analysis of Margarine.*" By CECIL H. CRIBB and P. A. ELLIS RICHARDS.

The paper deals with the application of the Reichert-Polenske process to the analysis of margarine containing cocoanut oil.

It is suggested that the process is capable of furnishing the necessary data for calculating the composition of such mixtures with fair accuracy if certain corrections, the need of which is explained, are applied to the figures obtained.

"*Observations on some Methods of Estimating Cocoanut Oil and Butter in Butter and Margarine.*" By CECIL REVIS and E. RICHARDS BOLTON.

Experimental evidence is adduced to show that the Reichert-Meissl-Polenske process alone will detect and approximately estimate down to 5 per cent of cocoanut oil in butter, when carried out under standard conditions. These values, together with the Kirschner value, admit of the detection of even 2 per cent of butter-fat in the presence of as much as 75 per cent or more of cocoanut oil, and will allow of the approximate estimation of both cocoanut oil and butter respectively, in all likely proportions in margarine mixtures.

"*The Estimation of Quinine as the Acid Citrate in certain Organic Liquids.*" By T. COCKBURN and J. W. BLACK.

The estimation of quinine in many substances, such as urine, &c., by the direct weighing of the quinine after extraction with solvents does not yield accurate results. The authors have confirmed Nishi's work, wherein the quinine in ethereal solution is precipitated by an ethereal solution of citric acid, and the acid citrate weighed. The method is inapplicable to the separation of the cinchona alkaloids.

"*The Determination of the Amount of Dissolved Oxygen Absorbed by Sewage Effluents containing Nitrites, and of the Amount of Nitrite in Sewage Effluents or Water.*" By R. W. CLARKE.

The difficulty in obtaining a satisfactory end-point with Winkler's manganous chloride and alkaline iodide method (*Ber.*, xxi., 2843; xxii., 1764) in the presence of nitrites is avoided if the free acid be neutralised with magnesium carbonate before titration with thiosulphate. The reaction is applicable to the determination of nitrites, dissolved oxygen being removed by sedimentation after the addition of manganous chloride and alkaline iodide, an aliquot portion of the clear supernatant fluid being acidulated with hydrochloric acid, and the liberated iodine titrated with thiosulphate after neutralisation of the excess of free acid with magnesium carbonate.

RÖNTGEN SOCIETY.

AT the meeting of the Röntgen Society on June 1st, Mr. C. W. RAFFETY, F.R.A.S., read a paper on the "*Photographic Action of Electrical Discharges in Air at a Pressure below that of the Atmosphere.*"

The sparks were produced by the ordinary method of using an induction coil, one terminal of the secondary winding being connected with a metal-point brought down centrally on the sensitive film of the photographic plate, which was in a bell-jar, and the other terminal joined to the metal plate on which the photographic plate rests. The coil used in Mr. Raffety's experiments had a spark of 2 to 3 cm. between points in air of normal pressure, and the plate was placed at an angle of 45°, the electrode meeting it being bent at a corresponding angle so as to come down upon it more vertically than would otherwise be the case. Taking first the discharges in which the point electrode in contact with the film was positive, Mr. Raffety found that the size of the spark increased rapidly as the pressure was reduced. The filaments lengthened and broadened, and each retained its own individuality in spite of the frequent intersections. With pressures below 100 mm. a glow type of discharge began to be suggested, and one negative at a pressure of 38 mm. showed the transitional condition between the spark and the glow. The negative discharges at atmospheric pressure had the characteristic palm-leaf structure, and with a state of increasing vacuum this gave way to a crab-like appearance with a sickle formation which reappeared continually as the pressure was reduced. Indeed, popularly, the positive discharges were called spiders and the negative discharges crabs. Discussing the point as to whether the presence of the photographic plate altered the spark, Mr. Raffety said that his experiments indicated that it did not. The discharge did not appear to take place through the substance of the plate, but above its surface.

Mr. A. A. CAMPBELL-SWINTON, Mr. W. DUDDELL, and others took part in the discussion, and one speaker, Dr. HORACE MANDERS, spoke of the remarkable similarity between the figures obtained in electric discharges and the pictures of the nebulæ, particularly those of Orion, seen through the telescope. He suggested that in the future, instead of regarding the nebulæ as masses of glowing gas, they would think of them as actual discharges of negative electricity, their individual shapes taking form according to the degree of vacuum or pressure in which they occurred.

Faraday Society.—On Tuesday, June 13th, at 8 p.m., Prof. Ernst Cohen, of the University of Utrecht, will give an illustrated lecture before the Faraday Society on "Allotropic Forms of Metals." Prof. T. W. Richards, of Harvard College, has been invited to take the Chair on this occasion. Applications for tickets should be made to the Secretary, 82, Victoria Street, London, S.W.

NOTICES OF BOOKS.

A Practical Guide to Iron and Steel Works Analyses. By WALTER MACFARLANE, F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911. (4s.).

THIS book is an abridgment of the author's "Laboratory Notes on Iron and Steel Analyses," and will, no doubt, be found as valuable as that excellent work. It contains very concise and clear directions for determining the most important constituents of steel and pig-iron, and for analysing samples of limestone and of solid fuels. The book is well adapted for use in the laboratory, and if the instructions are exactly followed the student will have very little chance of going wrong in performing his analyses, while his work will be so dovetailed in that he will make the best possible use of his time; the author having had a very long experience of the work of a steel works laboratory, can speak authoritatively as to choice of methods and the best way of carrying them out. Fully worked-out examples are introduced to show clearly the way to calculate and state the results of analyses.

The Green Book of London Society. London: J. Whitaker and Sons, Ltd. 1911.

THE new issue of the "Green Book of London Society" contains a directory of British titles, which is practically an index to the Peerage, and in addition many lists of officials, leading authors, artists, scientific men, &c. The section on sports and hobbies has been greatly enlarged, and the articles on the different branches—aeronautics, motoring, racing, and others—have been thoroughly revised by eminent authorities.

Hydrocarbures, Alcools, et Ethers de la Série Grasse ("Hydrocarbons, Alcohols, and Ethers of the Fatty Series"). By P. CARRÉ. Paris: Octave Doin et Fils. 1911. (5 francs).

THIS volume belongs to the Bibliothèque de Chimie, which forms part of the Encyclopédie Scientifique published under the editorship of Dr. Toulouse. The Bibliothèque de Chimie is to treat only of pure chemistry, and is to present all the useful features of a dictionary of chemistry without its inconveniences; this volume seems to be a worthy addition to those which have already been published. It gives full details of the preparation and properties of the fatty hydrocarbons, alcohols, and ethers, including the organic derivatives of sulphur, selenium, and tellurium. The text is methodically arranged, and the details appear to be accurate and to embody the results of recent research. The book contains an excellent bibliographical index, and its good get-up and moderate price will recommend it to students.

CORRESPONDENCE.

SMELTING OF MATERIALS CONTAINING LEAD.

To the Editor of the Chemical News.

SIR,—With reference to the Home Office circular letter of February 14th last, enclosing a draft of Regulations proposed to be made under Section 79 of the Factory and Workshop Act, 1901, for the smelting of materials containing lead, the manufacture of red or orange lead, and the manufacture of flaked litharge, I am directed by the Secretary of State to inform you that, after consideration of the objections received by him, he has decided to make certain amendments in the Regulations as drafted, in order to meet difficulties which have been pointed out by persons affected. He is glad to find that these amendments can be made without materially affecting the usefulness of the Regulations, and that with the alterations, the Regulations are likely now to be accepted without further objection.

The provisions of the Act, however, require that the draft shall be re-published as amended, and the Secretary of State accordingly gives the following formal notice:—

"That he proposes to make Regulations, dealing with the smelting of materials containing lead, the manufacture of red or orange lead, and the manufacture of flaked litharge, in accordance with the enclosed draft, copies of which may be obtained on application to the Factory Department, Home Office, London, and that any objection with respect to the draft Regulations by or on behalf of any person affected thereby, must be sent to the Secretary of State within twenty-one days of this date. Every such objection must be in writing and must state (*a*) the draft Regulations or portions of draft Regulations objected to; (*b*) the specific grounds of objection; and (*c*) the omissions, additions, or modifications asked for.—I am, &c.,

EDWARD TROUP.

Home Office, Whitehall,
June 2nd, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 5, 1911.

Experiments to Prepare Optically Active Phosphorus Compounds. — Fritz Ephraim.—Phenylamidophosphoric acid, $PO(NH_2)(OH)(OC_6H_5)$, cannot be split up into optically active components, and hence the ionogen complex $PO_2(NH_2)(OC_6H_5)$ cannot contain an asymmetric phosphorus atom. The sulphur compound, phenylamidosulphophosphoric acid, $SP(OC_6H_5)(NH_2)OH$, also resists all attempts to split it up into active components.

Atti della Reale Accademia dei Lincei.
Vol. xx., No. 3, 1911.

Hydrated Addition Products of Metallic Bichromates.—G. A. Barbieri and F. Lanzoni.—The authors have prepared a series of crystalline compounds of the type $M''Cr_2O_7.7H_2O.2C_6N_4H_{12}$ where M'' = Mg, Zn, Mn, Co, Ni, by allowing hexamethylene tetramine in concentrated solution to act on a concentrated solution of the acetate or sulphate of the metal in question in presence of $K_2Cr_2O_7$. The compounds are decomposed by the action of light, the chromic acid being reduced.

Compounds of Salts of the Rare Earths with Hexamethylene-tetramine.—G. A. Barbieri and F. Calzolari.—By allowing hexamethylene tetramine to act on aqueous solutions of different salts of cerium, lanthanum, and neodymium, compounds of the types—

$$M'''Cl_3.14H_2O.2C_6N_4H_{12}$$
$$M'''(NO_3)_3.8H_2O.2C_6N_4H_{12}$$

are obtained; with yttrium and erbium the compounds have the formulæ—

$$M'''Cl_3.11H_2O.2C_6N_4H_{12}$$
$$M'''(NO_3)_3.10H_2O.2C_6N_4H_{12}.$$

All these salts can readily be obtained in the crystalline state.

Ternary System Ag-Sn-Pb.—N. Parravano.—In this paper the author gives a graphic representation of the results of the study of the ternary system Ag-Sn-Pb.

Double Salts of Lead Fluoride and other Halogen Salts of Lead.—Carlo Sandonnini.—The author has

studied the system $PbCl_2$—PbF_2 to determine the eutectic points. He finds that a eutectic occurs at a concentration of about 10 molecules per cent of PbF_2, and the curve reaches a maximum at a concentration of 50 molecules per cent of PbF_2. Another eutectic point occurs at 75 molecules per cent of PbF_2.

Action of Cyanguanidine on Amides.—A. Ostrogovich.—Cyanguanidine condenses with acetamide chlorhydrate, giving a yield of 65—70 per cent of the theoretical amount of methyldiamino-triazine. An equally good yield of phenyl diamino-triazine is obtained by the condensation of cyanguanidine with benzamidine chlorhydrate.

Vol. xx., No. 4, 1911.

Direct Synthesis of Glycerides.—I. Bellucci.—The direct synthesis of common glycerides can be effected with an almost theoretical yield at 200—250° at the ordinary pressure from the stochiometric quantities of fatty acid and glycerin, if the water generated by the reaction is eliminated and the atmospheric oxygen is removed by a current of an inert gas.

Structural Isomerism in Metallic Cyanides.—I. Bellucci and G. Sabatini.—The authors have further investigated the properties of the α and β-potassium ferricyanides. The α-ferricyanide gives Pinner's reaction, while the β-ferricyanide does not; hence the former has probably the nitrile constitution $Fe(-C\equiv N)_6K_3$, while the β-compound is the isonitrile $Fe(-N=C)_6K_3$. The α- can be converted into the β-form by the action of hydrogen ions, and the inverse change is induced by hydroxyl ions. The β-ferricyanide is the labile form.

Esterification of Isoxazolones with Diazomethane.—E. Oliveri-Mandala and A. Coppola.—When methylisoxazolone condenses with diazo-methane two ethers are obtained, one in which the radical is united to the nitrogen and which melts at 74°, while the other melts at 163—164°, and has the radical united to the carbon. Phenyl isoxazolone yields an ether of melting-point 77—78°, and an oxymethyl ether which fuses at 70°.

Action of Nitriles on Cyanguanidine.—A. Ostrogovich.—When acetonitrile acts on cyanguanidine in a closed tube at 225—230° methyldiaminotriazine is formed, the yield being about 56 per cent of the theory; when benzonitrile at 190—200° is used a 60 per cent of phenyldiaminotriazine is obtained. With *p*-tolyl nitrile the hitherto unknown *p*-tolyl diamino triazine appears to be formed, and phenylacetonitrile condenses with cyanguanidine to give benzyldiaminotriazine.

Double Salts of Lead Fluoride and other Halogen Salts of Lead.—Carlo Sandonnini.—From the solidification curves of mixtures of lead fluoride and lead bromide it appears that two compounds are formed, $PbF_2.PbBr_2$ and $PbF_2.4PbBr_2$. The systems $PbCl_2 - PbF_2$ and $PbI_2 - PbF_2$ yield the same two compounds.

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Observations on Cotton and Nitrated Cotton," by H. de Mosenthal. "Methods of Testing Inflammable Gas and Vapour Detectors," by A. Philip and T. Stenhouse. "New Form of Automatic Detector of Inflammable Gases and Vapours," by A. Philip and L. G. Steele.
ESDAY, 13th.—Faraday Society, 8. "Allotropic Forms of Metals," by Prof. Ernst Cohen (Utrecht).
HURSDAY, 15th.—Chemical, 8.30. "Alleged Complexity of Tellurium," by A. G. Vernon Harcourt and H. B. Baker. "Purification and Properties of Acetic Acid," by W. R. Bousfield and T. M. Lowry. "Cupriglycollates," by S. U. Pickering.

ERRATUM.—P. 255, col. 1. Lines 31 and 32 from bottom as printed were transposed, and should read thus:—"and it is not too much to say that prosperity as an industrial nation is the only prosperity which we can hope."

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FIG. 1

FIG. 2

FIG. 3

FIG. 4.

FIG. 5.

FIG. 6.

FIG. 7.

THE CHEMICAL NEWS.

Vol. CIII., No. 2690.

THE AMOUNT OF RADIUM CONTAINED IN SOME URANIUM ORES.

By W. MARCKWALD and AL. S. RUSSELL.

As radium is formed from uranium, with uranium X and ionium as intermediate products, and decays with a mean duration of life of less than 3000 years, the proportion of radium to uranium in the uranium ores should be constant. As a matter of fact, Boltwood (*Phil. Mag.*, 1905, vi., 9, 599) and Strutt (*Proc. Roy. Soc.*, 1905, lxxvi., 88) have established the constancy of this ratio for a great number of ores. But Mlle. Gleditsch (*Comptes Rendus*, 1909, cxlviii., 1451; cxlix., 267) has recently investigated the ratio of radium to uranium in thorianite, Joachimsthal pitchblende, and autunite, and has obtained values which are in the proportion 100 : 85 : 68.

Since this question is obviously one of great theoretical importance, it seemed to us that it would be interesting to subject it to further study. Soddy, in collaboration with Pirret (*Phil. Mag.*, 1910, vi., 20, 345) also attacked the problem simultaneously. In agreement with these authors we have obtained the result that the ratio of radium to uranium in thorianite and Joachimsthal pitchblende is the same, differing, however, widely from that in autunite (Russell, *Nature*, August 25, 1910). A more thorough study of the subject has enabled us to discover the cause of this difference. We shall report fully on the details of the investigation elsewhere, and give here only the most important results.

Boltwood (*loc. cit.*) determined the radium in the uranium ores by dissolving the ores in nitric acid and measuring the emanation evolved by means of its ionising power. E. Gleditsch does not consider that this method is reliable, because the ores might contain traces of sulphur, which, when oxidised to sulphuric acid, would cause the separation of insoluble and non-emanating radium sulphate. She therefore recommends a very roundabout way, which possibly introduced an error into her measurements, for she precipitated the insoluble sulphates with sulphuric acid, converted them into carbonates, and used the solution of them in hydrochloric acid to measure the emanation.

Although neither thorianite, pitchblende, nor autunite actually contains appreciable amounts of sulphur, in the general application of Boltwood's method of measurement it seemed best by means of a simple device to make ourselves independent of any sulphate in the earth in the measurement of the emanation. This we did by dissolving the ore in concentrated sulphuric acid instead of nitric acid, with the addition of some crystals of saltpetre to act as an oxidising agent. Concentrated sulphuric acid dissolves barium sulphate and also radium sulphate easily, so that the emanation escapes quantitatively on heating the solution. We convinced ourselves of the accuracy of the method by a great number of experiments.

Our investigation extended to the following ores :—

1. Joachimsthal pitchblende.
2. Crystallised pitchblende (German East Africa) (W. Marckwald, *Zentralbl. f. Min.*, 1906, 761; *Thiel-Festschrift*, Berlin, 1909, 423).
3. Thorianite (Java).
4. Autunite (Autun).
5. Autunite (Guarda, Portugal).
6. Autunite (of unknown origin).
7. Rutherfordin (German East Africa).
8. Carnotite (Florida).
9. Carnotite (Colorado).

None of these ores contains appreciable amounts of sulphur. The measurements of the emanation were sometimes performed in nitric acid, sometimes in hydrochloric acid, and sometimes in concentrated sulphuric acid solution. The observations agree within a limit of error of about 2 per cent. Usually the emanation was expelled from the solution of the ore, and the emanation regenerated in a measured time was determined, because the ore may give up emanation when powdered. The percentage of uranium in the ore was determined in the usual way.

If the ratio of radium to uranium in Joachimsthal pitchblende is arbitrarily taken to be 100, we find that in thorianite it is 98·1, and in African pitchblende 101·5, which are values which agree within the limits of errors of observation. This is not the case with autunite, a calcium-uranyl phosphate of formula $Ca(UO_2)_2(PO_4)_2 + 8H_2O$.

We had at our disposal only a small, but very pure, piece of the ores 4 and 6. In the former we found the ratio of radium to uranium to be 27·7, and in the latter 60·7. We had larger quantities of the Portuguese autunite. It formed small yellow crystals, which were embedded in a large amount of gangue. The different pieces gave very different ratios of radium to uranium. Five specimens gave the following values :—20·7, 24·9, 38·6, 41·7, and 68·0.

Thus autunite usually contains only a fraction of the theoretical amount of radium. Now this mineral is distinguished by the fact which W. Marckwald and B. Keetman (*Ber.*, 1908, xli., 50) first pointed out, that unlike the other uranium ores it contains no appreciable amounts of lead, and, as Soddy (*Le Radium*, Oct. 7, 1910), recently reported, only very little helium. Hence it might be supposed that the mineral is so young that the formation of the decay products of uranium has not been completed. From the amount of helium in a crystal investigated by him, Soddy calculated that its age was only thirty years, assuming that the helium remained completely occluded. But as the amount of radium indicates an age of several thousands of years he assumes that the radium is not due to the decay of the uranium in the crystal, but has been introduced from without, and has been isomorphically mixed with the calcium double phosphate.

The assumption that minerals of this kind can be formed in shorter periods of time than thousands of years seems very improbable to us. Another explanation could be suggested, viz., that the mineral was much older than appeared even from the amount of radium it contained, but that in consequence of its spongy structure as compared with the very dense oxides like pitchblende and thorianite, not only is the occlusion of the helium very incomplete, but also the radium and the lead are partly extracted by water. This would also be an adequate explanation of the fact that the mineral from one and the same place contains such different amounts of radium.

We studied the question more thoroughly by investigating the amount of ionium contained in the ores. If Soddy's assumption is correct autunite must be almost free from ionium; if the amount of ionium corresponds with that of the radium the mineral must be several thousand years old; but if the amount of ionium is relatively higher than that of the radium our extraction hypothesis would be confirmed.

The determination of the ionium could not be performed with anything like the accuracy of the radium determination. We carried it out by precipitating the ionium from solutions of the ores by Marckwald and Keetmann's method (*loc. cit.*) by precipitating with hydrofluoric acid, with the addition of a little cerium, treating the precipitate with bisulphate, precipitating the oxides with ammonia, and finally dissolving in hydrochloric acid; thus a solution was obtained which was free from other radio-active substances except ionium, and contained only other earths. The solution was evaporated, and a very thin layer of the residue was tested with an electroscope. Experiments with Joachimsthal and African pitchblende showed that thus the amount of ionium was found to be roughly pro-

portional to the amount of uranium. The determinations differed from the mean by at the most 5 per cent.

If the ratio of ionium to uranium in these ores is taken to be 100, for the different specimens of autunite values are found which lie between 76 and 93, *i.e.*, the relative amount of ionium is appreciably smaller in the autunite, but is much more uniform in the different specimens than the amount of radium, and is always relatively very much higher. As ionium has a mean duration of life of certainly not less than 30,000 years, we must assume for autunite an age of at least some hundred thousand years.

As regards its occurrence, carnotite, a potassium-uranyl vanadate, resembles autunite. We have examined only two specimens of this ore, and found in the one 92 per cent and in the other only 72 per cent of the theoretical amount of radium. Lead could not be detected with certainty. The latter appears to be extracted more easily than radium, which is easily explained, since its salts are more soluble.

The investigation of rutherfordin, uranyl carbonate, $UO_3\,CO_3$, further confirmed our views. As W. Marckwald showed, this mineral resulted from crystallised East African pitchblende by pseudomorphosis. By comparing the γ-radiation of a large crystal which always contains more or less of a kernel of unchanged pitchblende with the radiation of a crystal of pitchblende of the same weight, it could be proved that in rutherfordin radium and uranium are present in the theoretical proportions. If a layer is shaved off the surface of a piece of rutherfordin, or if a specimen is investigated in which the formation of pitchblende has taken place only on the surface, it is found that the ratio of radium to uranium is much lower. We found in two experiments 86·8 per cent and 83·5 per cent.

The study of the percentage of lead shows much more clearly the effect of the extraction process, which takes place throughout the whole of the mass; for specimens of rutherfordin, the pitchblende kernels of which usually contain 7·1 to 7·5 per cent of lead oxide, only gave 1·0 to 1·3 per cent of lead oxide.

We owe hearty thanks to Prof. Lacroix, of Paris, Dr. O. Hauser, and Dr. Heidenrich, jun., of Berlin, for sending us valuable specimens of minerals.

CONTRIBUTIONS OF CHEMISTRY TO SANITATION.*

By Dr. W. P. MASON, Professor of Chemistry in the Rensselaer Polytechnic Institute, Troy, N.Y.

SINCE the radical changes in methods of analysis inaugurated by Frankland and Wanklyn were first presented, the alterations in chemical procedure have been rather of the nature of modifications than the introduction of new processes, or at least that is true for what may be termed "routine" water analysis.

Sundry of these modifications have been very acceptable, such as the statement of "turbidity" and of "colour" in "parts per million," rather than in descriptive words as of old, and also such as the quick methods for detection and determination of the metals. Weston's method for manganese is an instance in point, and the use of "formaldoxime" to detect copper in solution is another. The latter is especially useful since the employment of copper sulphate for destruction of algal growths has become so frequent.

The examination of water for the presence of the heavy metals is certainly more often undertaken than it used to be, and there is a growing feeling that it is wise to go beyond a simple statement of what metal is actually present in the sample at the time of analysis, and to determine what the water in question would do in the way of acting upon the common metals should it come in contact with them. In other words, there often is great value lying in a foreknowledge of just what may be expected should some certain water be sent through pipes of specific character. For that reason it is the part of wisdom to experimentally test the action of a water upon sundry metals, and to state the result as a note to the analytical report.

Although we know, in a general way, that softness, acidity, dissolved gases, and the presence of much chloride or nitrate will tend towards metallic action, while alkalinity and hardness are rated as protective agents, yet it is far better to actually test a water with reference to its behaviour towards metals than to attempt any prophecy of what it will do based upon analytical knowledge of its contents. And we may add that the rate of action of the same water is not only variable, but the ratio of the total action during different lengths of time is not a simple one. Thus the quantity of metal attacked in ten hours is by no means ten times that acted upon during one hour.

In one particular chemistry has shed no recent light upon the subject of water analysis, and that is in the matter of testing for "chlorine." Knowing as we do that chlorine forms a part of every pollution from sewage inflow, it would aid us greatly did we have a reliable means of detecting small variations in the quantity of it present. When we recall the great delicacy of some of the other tests in a routine water analysis we are struck by the comparative crudeness of what is available for chlorine. If some really delicate test for it were at hand then closer estimation of the amount of "cyclic salt" could be had, better maps of "normal chlorine" would result, and a needed revision of the *per capita* influence of population upon a water-shed would follow.

"Hardness" determination is another item with which the water analyst is not entirely satisfied, but the necessity for close accuracy is not so important in this case, as is shown when we consider the difficulty of interpretation. The question, "What is a hard water?" is not an easy one to answer. Of course, waters lying near the extremes of "hardness" and "softness" may be readily classified, but there is a pretty broad middle zone where doubt begins to appear, and one is forced to conclude that personal likes and dislikes enter very largely into the question.

After looking into the hardness of many waters on the Atlantic coast, the writer finds that the users of those waters are possessed of great variety of opinion touching the merits of their several supplies; for instance, a hardness of 41 parts per million is rated as "a little hard, but good for washing"; a hardness of 31 as "good for boilers, but not entirely satisfactory for washing"; a hardness of 46 as "very good"; another hardness of 46 as "not satisfactory"; a hardness of 63 as "too hard for boilers or laundry"; and a hardness of 70 as "complaint from laundries only."

From a consideration of expressions of opinion such as quoted, the reasonable division would seem to be to class as "soft" all waters below 50 in hardness, to call "hard" those that run as high as 100 or more, and to leave the space between these numbers as a kind of debatable ground wherein individual views shall govern.

When we come to protective measures for the general improvement of public waters, chemistry is now doing much more than simply furnishing the clarifying dose of alum; a means of improvement known to the ancient Egyptians. Copper sulphate, ozone, bleaching-powder, and the other hypochlorites are among the resources to which the water purveyor may turn for relief in the event of difficulty.

At the time copper sulphate was first proposed as a chemical cure for stopping the plague of taste-producing algæ, comment was made regarding the remark of a veteran water engineer who once said:—"No one who can row a boat should fear trouble from algæ." What the old man meant we now can only guess, but it may have been

* Abstract of a Lecture delivered before the New York Section of the American Chemical Society, March 17, 1911.

that he possessed the secret of "coppering" reservoirs, and carried his information with him to the grave. How useful copper sulphate is in curing objectionable plankton tastes is now widely known, nor is the "coppering" of water restricted to the killing of algæ alone. The process is in use for the destruction of bacteria during times of epidemic disease, although, in the opinion of the writer, ordinary bleaching-powder is a much more certain agent for such work. Within a few weeks past some 19 pounds of copper sulphate per million gallons of water have been added to the supply of a western city during an outbreak of typhoid, and the results have not been as beneficial as expected. Without doubt less than half that dose of ordinary "bleach" would have proved much more satisfactory.

Since the introduction of "bleaching-powder" three years ago for the purpose of ridding water of pathogenic organisms, the method has grown so in popularity that today it is not too much to say that practically all the new filter plants in course of erection have added to them devices for the introduction of "bleach" should occasion suddenly demand its use. What this chemical will do in the way of killing intestinal organisms is now a matter of common knowledge, and it would seem to be an unwarranted assumption of risk to fail to provide means for quickly supplying it in event of necessity. In this connection it should be said that "bleach" is especially serviceable under those unfortunate conditions when, because of some accident, the regular water supply is cut off and temporary recourse is had to an inferior supply for the purposes of providing fire protection.

"Emergency" intakes are always sources of danger, and many a life has been sacrificed through filling the mains with dilute sewage to guard against fire losses, as is instanced in the typhoid outbreaks of Butler, Lowell, Toronto, and many another town. Judicious use of the hypochlorites during these "emergency" periods will remove threatened danger, and is infinitely better than trusting to a notice to "boil the water"—advice which the careless portion of the community will never follow.

Ozone is another product for water purification which, on purely æsthetic grounds, is very acceptable to the masses, inasmuch as it is in their minds simply "electrified air." It is efficient, and will do all that is claimed for it, but can we afford its use? The weak points connected with the use of ozone are—first, its cost; second, the liability of the apparatus to get out of order. These objections will doubtless be overcome in time, and are reported by those interested as being already overcome. But we lack a collection of data upon a large scale. What we need is a municipality willing to take the risk of erecting a large plant operated upon the ozone system. We should all be delighted to study the results, and we should be glad to congratulate such a city in the event of success, and to use the information accumulated; but would we be entirely disposed to share the expenses in the event of failure? On the whole, while we admit the efficiency of ozone, and while we look hopefully towards its practical success in the future, we cannot but feel that at the present moment, with the meagre data we now possess, we should run considerable risk in recommending its introduction as a means of purifying a municipal water supply.

As has been already intimated, it is exceedingly difficult for the chemist to stand alone when considering sanitary problems. His field of inquiry continually overlaps those of other scientific men, and he requires their assistance to complete his work. This is especially true in water investigations, wherein, as has been said, bacteriology becomes so vitally important on both the qualitative and quantitative sides. When a water expert undertakes the solution of some important water problem he has only begun his task when he has secured a chemical analysis of the supply in question. He must of necessity supplement this with a bacteriological examination, and it may be he will also have to call microscopy to his aid in order to settle questions touching the presence of local plankton involving a study of the production of taste and smell.

Of course such matters as the building of reservoirs, conduit lines, and similar structures are relegated at once to the civil engineer, but some small knowledge of the fundamental principles of hydraulics must be comprised in the mental equipment of the water specialist in order that he may properly deal with the occasional questions which legitimately fall to him for answer. For instance, within six weeks past, while investigating a serious typhoid epidemic, the writer had occasion to call the attention of the city commissioners to the certainty of foul water reaching the general supply should a leak occur in the conduit line laid on the bottom of a sewage polluted bay. The commissioners were confident that no inflow could take place in the event of a leak because of their supposition that the water in the conduit was under pressure, a view which was manifestly in error, for there was no more possibility of internal pressure than there is in the case of a slightly inclined leader taking water from a roof. It would have been unfortunate to have interrupted the investigation until an engineer's opinion could have been secured upon so simple a matter.

It is not expected that the water specialist shall draw so largely from the science of medicine as to be able to sit by the bedside and treat a case of typhoid fever, but it is essential that he know something of the longevity of the typhoid organism, be acquainted with the conditions under which it is likely to give trouble, and be prepared to rectify them. He touches the outer boundaries of those fields of science with which his daily work brings him in contact, but he does not presume to seriously enter them, and when he needs information as to what they contain he applies for aid to those who know.

Allow me to quote from an editorial in a recent number of the *Engineering News*, dealing with the proposed law for licensing engineers:—

"The State proposes to grant a license to a man to practice civil engineering and to declare under the official seal of the State that the man is 'properly qualified to practice civil engineering,' which the law defines to be any branch of the profession of engineering other than military!" There is about as much sense in such a proposition as there would be in declaring under the State's official seal that a man was properly qualified to keep a hotel, run a steam shovel, act as cashier of a bank, fill teeth in a dentist's office, and practice law.

"No reputable and honest engineer, no matter how eminent in the profession, would dream of claiming himself competent and qualified to practice in all branches of the engineering profession."

The engineer's profession is large and varied. So is chemistry, and so is sanitary science. No man can begin to cover the modern field in any one of these callings, and when in the practice of his profession he finds, as he is sure to do, the more or less frequent interjection of questions foreign to his speciality, the only relief possible for him is to seek aid from those of his fellow scientists who have had experience in such problems as the one at hand. There is an interdependence of specialists which is constantly growing more pronounced in view of the ever widening field of knowledge, and a part of the equipment of a successful man lies in his knowing just where to secure the kind of aid he needs, where to find the right man to join him in the work of a commission, where to get, first hand, that collateral accurate information which it would be so tedious and difficult for him to obtain for himself.

In view of the existence of what was above termed the "interdependence of specialists" is it not patent that a sort of chemical clearing house is needed, and that a club like this supplies the want? Here men of many forms of professional activity are at home, and here they may exchange their views with mutual benefit; not always in the form of critical reviews of formal papers, but often in that more valuable type of discussion, namely, the intimate and friendly chat upon topics of common interest.

One of the greatest contributions that chemistry has made, not only to sanitary science, but to all branches of the broad chemical field, is epitomised in the erection of this beautiful and most useful building as the central home for the chemists of America.

ORGANIC AMALGAMS: SUBSTANCES WITH METALLIC PROPERTIES COMPOSED IN PART OF NON-METALLIC ELEMENTS.*

By HERBERT N. McCOY and WILLIAM C. MOORE.

(Concluded from p. 269).

E. *Discussion of the Potential Measurements.*

On examining the two curves, it is seen that their forms are very interesting. In 209 B, where the electrolyte was half-normal tetramethyl ammonium chloride, in absolute alcohol, the potential remained eonstant for some time after the polarising current was interrupted. This constant value was about 2·62 volts; after awhile, however, the potential dropped rapidly to a new value near 2·00 volts.

In 233 B, with water as the solvent for the half-normal tetramethyl ammonium chloride, the average value of the potential, while the current was on, was about 2·4 volts, but on cutting off the polarising current the potential dropped to about 2·0 volts immediately, then gradually fell to 1·6 volts, and in the end quickly dropped to almost zero.

The horizontal or nearly horizontal portions of these curves can have but one interpretation; a definite phase of the amalgam gives rise to a definite potential; and when this particular phase is exhausted, if there is a different phase possible, the potential drops to that of the new phase. Hence, in 209 (as in 205 and 206, as will be seen by plotting curves for these experiments) there were formed at least two phases; one may be the decomposition product of the other, or they may be coincident in the amalgam, the more active disappearing first.

Now, Wilsmore and Johnson (*Elektrochem. Zeit.*, xiv., 203) have recently shown that for the electrode potential of metal, using as a solvent, for the salt of the metal, liquid ammonia at $-35·5°$, a higher value is obtained than when water is the solvent. They account for this fact on the assumption that the degree of ionisation is less in liquid ammonia than in water solutions of equivalent concentrations. This explains why, in the present instance, the electrode potential of one of the phases stable in contact with absolute alcohol solutions of tetramethyl ammonium chloride is 2·6 volts, while in contact with an aqueous solution of the same salt in equivalent concentration the potential averaged about 2·40 volts. The two values, 2·6 volts in alcoholic solution and 2·4 volts in aqueous solutions of tetramethyl ammonium chloride, are obviously due then to the same phase, but when the polarising current is cut off where water is the solvent the potential immediately falls, because this phase is very reactive towards the water. Likewise, the phase showing a potential of 2·0 volts in experiment 209 must be the same which shows a potential of 1·74 volts (average) in experiment 233, but this phase is likewise less stable in contact with water than alcohol, as is shown by the slowly but constantly changing values in 233 B.

The high polarisation values in experiments 205 and 206 are probably due to a still more active phase which did not appear in experiment 209.

These experiments do not afford the only proof at hand that more than one phase of the amalgam is formed. Throughout this work it has been noticed that immediately under the anode the amalgam formed has a more solid, more crystalline appearance and a darker colour than the rest of the amalgam; in experiment 300, a portion of amalgam practically solid was formed. Again, when the amalgam is treated with water the first action is violent, and the whole of the reaction mixture becomes inky-black, quickly turning to the grey colour of ordinary colloidal mercury. On treating the amalgam with water in a flat dish and washing away the colloid by means of a stream of water as fast as it is formed, a darker, more solid phase, floating on the mercury, has been noticed. While this phase still reacts with water to form the colloidal mercury, it is less active than the main portion of the amalgam.

The existence of these various phases may explain why no constant values for the ratio of the colloidal mercury to the tetramethyl ammonium group have been found, as each run has obviously been a mixture of a number of phases in varying proportions.

It will now be of interest to compare our results with those of Lewis and Kraus (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1459), just published, on the potentials of sodium and sodium amalgam, although we made no serious attempt at accurate definition of the potentials measured, while they attained a remarkably high degree of accuracy. For the cell:—Sodium amalgam (0·206 per cent), normal Na ion, normal calomel electrode, Lewis and Kraus found an electromotive force of 2·1525 volts at 25°, and for metallic sodium, normal Na ion, normal electrode, 2·9981 volts. In experiment 233, Table IV., we found for the cell:—Tetramethyl ammonium amalgam, 0·5 normal ion, 0·1 normal KCl, decinormal electrode, a maximum electromotive force of 2·57 volts at 0°. This would be equivalent to about 2·73 volts for conditions as in the experiments of Lewis and Kraus, excepting the concentration of the amalgam. The latter was not known in our experiment, but was probably in the neighbourhood of 1 per cent. It is, therefore, clear that the potential of our amalgam is decidedly greater than that of sodium amalgam of the same concentration, which conclusion is in harmony with the very much greater activity of our amalgam toward water and alcohol.

Reuter (*Zeit. Elektrochem.*, 1902, viii., 801) found that the potential of potassium is 0·4 volt higher than that of sodium at $-80°$, which would indicate a difference of 0·6 volt at 25°. As a rough estimate, then, the potential of our amalgam should be about the same as that of potassium. From the observed behaviour toward water, however, we should expect the potential to exceed that of potassium, but to fall somewhat short of that of rubidium. It is of passing interest, though of doubtful significance, that the molecular weight of tetramethyl ammonium, 74·1, falls between the atomic weight of potassium, 39·1, and rubidium, 85·45.

F. *Monomethyl Ammonium Amalgam.*

The polarisation measurements of Le Blanc (*loc. cit.*) indicated that an amalgam was formed by the electrolysis of an aqueous solution of monomethyl ammonium chloride. We had no difficulty in obtaining the amalgam. The electrolysis took place at ordinary temperature, with 0·25 ampère. The readily formed amalgam resembled ammonium amalgam in its properties. When a solution of *dry* monomethyl ammonium chloride in absolute alcohol was electrolysed (experiment 55) at ordinary temperature, at 0° and at $-9°$ amalgamation again occurred. At $-9°$ the amalgam formed was pasty. The potential of the cell:—*Monomethyl ammonium* amalgam, 0·5 N monomethyl ammonium chloride, 0·1 N KCl, 0·1 N calomel electrode was measured, exactly as in the method above for the tetramethyl ammonium amalgam. The solvent in 229 was water and in 231 was absolute alcohol. "Series A" in each case contains measurements made while the polarising current was on; "Series B" after the polarising current had been cut off.

On examining these results, it is seen that here the potentials in contact with alcohol are less than those where water is the solvent; it was found that a similar result was obtained with ammonium amalgam; indeed, the remark-

* Preliminary report read at the Detroit Meeting of the American Chemical Society, June, 1909 (*Science*, 1909, xx., 315). From the *Journal of the American Chemical Society*, xxxiii., No. 3.

able fact was discovered that ammonium amalgam is much more reactive toward absolute alcohol than toward water.

As tetramethyl ammonium amalgam was obtained very soon after this work was undertaken, almost immediately an extensive search for amalgams of other radicals was begun, with the hope that some might be found which would be more stable. Of eighteen additional radicals studied, only one, monomethyl ammonium, gave an amalgam which could be isolated. The others gave, in general, negative results. The salts so studied were: — Dimethyl ammonium chloride, trimethyl ammonium chloride, monoethyl ammonium chloride, tetraethyl ammonium chloride, propyl ammonium chloride, butyl ammonium chloride, iodomethyltrimethyl ammonium iodide, aniline hydrochloride, dimethylaniline hydrochloride, phenylenediamine hydrochloride, phenyldiazonium chloride, pyridine hydrochloride, tetraethylphosphonium iodide, tetramethylstibonium iodide, trimethylsulphinium iodide, hydroxylamine hydrochloride, and hydrazine hydrochloride.

Table V.—*Electromotive Forces in Volts.*

Time (mins.).	229 A.	229 B.
0	0·023	2·369
1	—	1·646
2	—	1·655
4	—	1·666
6	—	1·666
7	—	1·670
9	—	1·623
11	—	1·569
13	2·099	1·556
15	2·099	1·504
17	2·153	1·512
19	2·153	1·481
21	2·335	1·481
23	2·282	1·471
25	—	1·471
27	2·479	1·460
28	2·369	—
30	—	1·455
33	—	1·085
34	—	0·842

Time (mins.).	231 A.	231 B.
0	0·161	1·952
2	—	1·372
4	—	1·314
6	—	1·340
8	—	1·318
10	—	1·323
12	2·126	1·311
14	2·082	1·260
16	1·889	0·387
18	1·915	0·300
20	1·915	0·269
22	1·933	—
24	1·924	—
27	1·252	—

G. *Summary of Results.*

1. Tetramethyl ammonium amalgam has been prepared by the electrolysis in the cold of solutions of tetramethyl ammonium chloride in absolute alcohol, using a mercury cathode.

2. The amalgam exhibits certain physical properties of metals to a high degree. It has a crystalline structure more or less pronounced under certain conditions. It is lighter than mercury, but does not expand or become inflated at or below 10°, as does ammonium amalgam.

3. While fairly stable at low temperatures, near 20° it decomposes rapidly, yielding trimethylamine as one of the decomposition products.

4. In contact with cold air it becomes coated over with a white alkaline crust, due to oxidation.

5. Water reacts violently on the amalgam, producing hydrogen, colloidal mercury, and tetramethyl ammonium hydroxide.

A study of this reaction affords evidence that more than one active phase exists in the amalgam.

6. The amalgam acts on aqueous solutions of ammonium, sodium, potassium and copper salts, and alcoholic solutions of copper and zinc salts, the tetramethyl ammonium group replacing these metals in the salts and setting free the metals themselves or forming the amalgams of these metals. With rubidium and cæsium salts the action is more violent than with potassium salts of equivalent concentration, but there is replacement even in the case of the cæsium salts. The tetramethyl ammonium radical possesses a solution tension comparable with that of potassium, but probably less than that of rubidium and considerably less than that of cæsium.

7. The rate of formation of the tetramethyl ammonium ion from the amalgam, in contact with absolute alcohol, is about 5 per cent per minute at 0°.

8. The electrode potentials of the amalgam in contact with water solutions and in contact with alcoholic solutions of tetramethyl ammonium salts have been measured against a decinormal calomel electrode at 0°.

2·6 volts and 2·0 volts were the values of the electromotive force of the amalgam calomel electrode cell found in contact with alcoholic solutions; 2·4 and 1·7 volts were found in contact with aqueous solutions of tetramethyl ammonium salts as the values of these potentials. The two values in each case probably correspond to two phases, thus substantiating other evidence that more than one phase of the amalgam is present in the amalgam. The curves for these potentials have been plotted.

9. Besides the extensive work upon tetramethyl ammonium amalgam, search has been made for other possible amalgams. Of the substances investigated, the monomethyl radical yields an amalgam, and the potential of this amalgam against a decinormal calomel electrode has been measured. This amalgam, like ammonium amalgam, is less stable in contact with alcohol than with water. The dimethyl ammonium radical, according to potential measurements, may possibly form an amalgam under certain conditions. Tetraethyl ammonium probably forms a very unstable amalgam. Of all the other substances investigated, a number gave faint indications of amalgam formation, but none gave as positive results as the three substances mentioned above.

10. As set forth in the introduction, we have proposed the hypothesis that complex radicals, constituting the positive ions of salts, if electrically neutralised by the introduction of electrons, equal in number to the valence of the ion, will be substances having metallic properties. We have, however, given some reasons why it may be impossible to isolate such radicals. While our experiments have not yet led to the complete isolation of complex radicals, we have gotten a new amalgam of one such radical which is far more stable than either ammonium amalgam or monomethyl ammonium amalgam. Though this substance is a compound of carbon, hydrogen, and nitrogen on the one hand, and mercury on the other, it has true metallic properties. Inasmuch as ordinary binary alloys with true metallic properties are formed only from components which are *both* true metals, we are warranted, we think, in concluding that the organic radicals in our amalgams are in the metallic state, and, therefore, that *it is possible to prepare composite metallic substances from non-metallic constituent elements.*

Decomposition of Water by Ultra-violet Light.—A. Tian.—By the action of all the rays emitted by a quartz mercury lamp, water is decomposed into hydrogen and hydrogen peroxide, which itself decomposes and yields oxygen. After a certain time the action of the lamp is the same as that of electrolysis as far as the gases disengaged are concerned—*Comptes Rendus*, clii., No. 15.

VOLUMETRIC DETERMINATION OF POTASSIUM BY THE COBALTI-NITRITE METHOD.*

By O. M. SHEDD.

THE writer, in making some determinations on the fertiliser samples sent this year by the referee on potash of the Association of Official Agricultural Chemists, obtained such interesting results in using the cobalti-nitrite method as modified by Drushel (CHEMICAL NEWS, 1908, xcvii., 124) for the determination of potassium that it was decided to publish a summary of them, since they throw much light upon the best conditions for applying this method.

The accuracy of this method has been considerably discussed of late, and it has been considered of sufficient importance to have been recommended to the above-named association for co-operative work by the referee on potash, and also by the referee on soils.

Drushel in his original article had published some results obtained with this method on fertilisers, and recommended it for this purpose, and his method, with a slight modification by Bowser (*Journ. Industrial and Eng. Chem.*, i., 791), is the one proposed for study this year. On the other hand, the writer (*Ibid.*, i., 302) has proposed it in connection with the J. L. Smith method for the determination of total potassium in soils, and has obtained very good results in this manner. Later on, further work by the writer (*A. O. A. C. Proceedings*, 1909) and others was presented to the Association at its annual meeting last year with the result that this method has been taken up by the referee on soils. Incidentally, it might be of interest to mention that the writer has obtained very good results in using this method on the soils sent this year by the referee on soils for co-operative work.

In the method, as proposed for soils, a change was made in the outline as given by Drushel which, while it may seem of small importance, is very essential in the application of the method. Drushel had recommended that the solution (apparently not restricting the volume) at the proper point was to be slightly acidified with acetic acid, and a liberal excess of the sodium cobalti-nitrite reagent added and evaporated to a pasty condition on the water-bath. On the other hand, the writer in his article had recommended that the volume should be concentrated to about 5 to 10 cc. before adding the nitrite reagent. That this is the best condition under which to work will be shown later, and it is not necessary to discuss it here, except in a general way. The nitrite reagent being unstable at room temperature, and especially so on heating, the method that completely precipitates the potassium when the reagent is added with the minimum amount of heating, of course, is the one to be preferred. Again, when the dilution is too large, the nitrite reagent is all decomposed on heating before the potassium salt is precipitated, and consequently low results will be obtained. Finally, the potassium salt itself is acted on to some extent by the acetic acid and water present, and while it may precipitate at ordinary temperature, on heating the precipitate will disappear and the solution become pink. Therefore if at the end of the evaporation there is not an excess of the nitrite reagent present, low results will be obtained.

To illustrate the above points, a few qualitative tests might be given. The potassium salt was made by precipitating chemically pure KCl solution cold with an excess of the reagent, and washed with cold water by decantation. A portion suspended in water and heated in the boiling water-bath dissolved slowly, giving a clear pink solution after about two hours' heating. This solution evaporated on the water-bath in a dish left a blue residue. On taking up with cold water acidified with acetic acid, a notable quantity of the yellow potassium salt remained, perhaps about half of the original quantity, and the solution was pink. On repeating the evaporation and resolution a second and a third time, only traces of the yellow salt remained.

Another portion was suspended in water, and divided equally between two test-tubes. To one, a few drops of acetic acid were added, and the two heated side by side in the water-bath. The potassium salt disappeared much quicker in the one containing the acid than in the pure water. This experiment was repeated with the same result.

Another portion was allowed to stand at room temperature in contact with 2 or 3 cc. of water, shaking occasionally. After several days, the water became distinctly pink, showing decomposition of the yellow compound.

Another portion was let stand at room temperature in about 50 cc. of water, with occasional shaking. At the end of a month, all but a trace of the yellow compound had disappeared. On evaporating part of the clear liquid at room temperature over sulphuric acid, there remained a yellow residue, apparently consisting mostly of the potassium double salt, but mixed with pink needle-shaped crystals, having the appearance of a cobalt salt.

A little of the reagent diluted with 10 or 15 times its volume of water, and heated on the water-bath, soon lost its brown colour, and became pink, showing complete decomposition of the reagent. An equal portion treated in the same manner, except that several drops of acetic acid were added, underwent the change more quickly. The greater the dilution the quicker this change takes place.

Upon evaporating the reagent to dryness after diluting with water, as in the above experiment, the mass is distinctiy purple in colour, and upon adding water there remains an insoluble greenish residue containing cobalt, while the solution is pink. The characteristic colour of the reagent has entirely disappeared, which indicates complete decomposition.

To prove that this greenish substance will have the same effect as the potassium salt, if it should be present, the following tests were made:—Two 10 cc. portions of the reagent were diluted to 15 times their volume, and then evaporated until the contents of one was pasty on cooling. The other was further evaporated until the contents were just dry and firm on cooling. They were then taken up with water, filtered, and treated with permanganate and oxalic acid in the same manner as the potassium salt in the method. The following results were obtained:—

Contents on cooling.	N/10 $KMnO_4$. required in titration.
	Cc.
Pasty	1·74
Dry	3·08

The above results show that if these same amounts of this substance were present in two determinations worked like the above on 0·10 grm. aliquots of a potassium salt, the results would be too high to the extent of 1·50 per cent and 2·64 per cent K_2O in the respective determinations.

These tests show that too great a dilution should be avoided, because it decomposes the reagent, and also continued heating in the evaporation should be avoided, because in the final stage of evaporation the last traces of acetic acid may be expelled, and as soon as this takes place the greenish substance is formed more rapidly than it would be if there still remained some free acid.

To show that the above holds true, two 5 cc. portions of the reagent were diluted to 15 times their volume, and evaporated until the volume of one was about 5 cc. and liquid on cooling. The other was evaporated until pasty on cooling. When water was added to both, there was a small amount of the greenish residue in the first, but considerably more in the other.

This source of error could be avoided in the work if a few drops of acetic acid were added to the solution before filtering, as this readily dissolves this substance and would leave the potassium salt practically pure.

The above experiments show that both the cobalti-nitrite reagent and the yellow potassium compound are decomposed by heating with water, and that the change is hastened in the presence of acetic acid.

* *Journal of Industrial and Engineering Chemistry*, ii., No. 9.

The samples sent by the referee on potash were three in number, namely, commercial muriate, kainit, and a complete mixed fertiliser. The directions called for a study of the cobalti-nitrite method in comparison with the official platinum method. The aliquots recommended for the volumetric method were 0·10 grm. for the muriate, 0·5 grm. for the kainit, and 1 grm. for the mixed fertiliser. These aliquots were used in all of the determinations. The directions also called for the volume of the solution to be about 25 cc., when 1 cc. glacial acetic acid and 10 cc. recently prepared nitrite reagent were to be added, and the evaporation made.

The referee's directions were followed in the determinations below, the aliquots for the two methods being taken from the same solution. In the volumetric method the solutions were heated until the contents were just dry and firm on cooling.

	K_2O found (grm.).	K_2O found (per cent).
	Official Method.	
Muriate	0·26025	52·05
	0·25980	51·96
Average ..	0·26005	52·01
Kainit	0·06380	12·76
	0·06435	12·87
Average ..	0·06410	12·82
Fertiliser	0·04660	4·66
	0·04660	4·66
	Cobalti-nitrite Method.	
Muriate	0·04928	49·28
Kainit	0·05930	11·86
Fertiliser	Not determined	—

It was apparent that the referee's directions had a tendency to give low results, probably due to the volume being too large when the nitrite reagent was added. To see if an increase of the amount of reagent added at that volume would recover the potassium present, the following determinations were made on the muriate:—

	K_2O found (grm.).	K_2O found (per cent).
10 cc. nitrite added ..	0·04928	49·28
15 ,, ..	0·05022	50·22
20 ,, ..	0·05125	51·25

The following determinations were made by evaporating the solution to about 5 cc. before adding the acetic acid and nitrite reagent. The reagent was added in various amounts, and dishes heated until residues were of the consistency as noted on cooling.

Nitrite. Cc.	K_2O found. Grm.	K_2O found. Per cent	Contents on cooling.
		Muriate.	
10	0·05159	51·59	Dry.
10	0·05151	51·51	Dry.
15	0·05223	52·23	Dry.
15	0·05155	51·55	Dry.
15	0·05169	51·69	Dry.
15	0·05142	51·42	Very dry.
15	0·05142	51·42	Pasty.
15	0·05159	51·59	Thick paste.
15	0·05134	51·34	Very thin paste.
25	0·05095	50·95	Dry.
25	0·05108	51·08	Pasty.
		Kainit.	
15	0·06280	12·56	Dry.
15	0·06360	12·72	Dry.
15	0·06230	12·46	Very dry.
15	0·06315	12·63	Very thin paste.
25	0·06355	12·71	Dry.
25	0·06345	12·69	Pasty.
15	0·05382	53·82	Dry.
15	0·05347	53·47	Dry.
15	0·05458	54·58	Dry.
15	0·05453	54·53	Dry.
15	0·05390	53·90	Pasty.
15	0·05390	53·90	Pasty.
15	0·05399	53·99	Pasty.
		Mixed Fertiliser.	
25	0·04680	4·68	Pasty.
25	0·04630	4·63	Pasty.

In following the directions of the referee in the above work, the dishes were heated until the residues were syrupy while hot and just dry and firm on cooling. According to Drushel, this is the best plan to follow, for it thus avoids errors in the continued heating of the residues which will vitiate the results. This was done regardless of the time consumed, which was noticed varied in similar determinations and very often with different salts.

After some correspondence with the referee, who stated that the method as outlined by him generally gave satisfactory results in his hands, the writer made some further determinations on the samples, and also on chemically pure salts. In this work, the referee's directions were followed, and also the modification as stated above, whereby the solution was concentrated to about 5 cc. before adding the nitrite reagent. The time consumed in the evaporation after adding the nitrite reagent and the consistency of the contents on cooling after the evaporation was made were also noted. The evaporations were made in casseroles of 750 cc. capacity, except in the case of the kainit, when 400 cc. casseroles were used.

Referee's Directions.

Time. Mins.	K_2O found. Grm.	K_2O found. Per cent.	Contents on cooling.
		Muriate.	
45	0·05187	51·87	Thin syrup.
45	0·05226	52·26	Thin syrup.
45	0·05179	51·79	Thin syrup.
45	0·05145	51·45	Thin syrup.
	Average	51·84	
40	0·05145	51·45	Thin paste.
40	0·05136	51·36	Thin paste.
45	0·05104	51·04	Thin paste.
45	0·05159	51·59	Thin paste.
	Average	51·36	
60	0·05119	51·19	Dry.
60	0·05110	51·10	Dry.
	Average	51·15	
		Kainit.	
50	0·06300	12·60	Pasty.
60	0·06345	12·69	Pasty.
60	0·06285	12·57	Pasty.
	Average	12·62	
90	0·06275	12·55	Dry.
	Chemically Pure KCl—*Theory*, 63·17 *per cent* K_2O.		
20	0·05093	50·93	Liquid about 15 cc. vol.
45	0·06108	61·08	Thin syrup.
45	0·06358	63·58	Thin syrup.
45	0·06283	62·83	Thin syrup.
70	0·06342	63·42	Pasty.
70	0·06325	63·25	Pasty.

The determinations below were made by having the volume about 5 cc. when the nitrite reagent was added, and 15 cc. of this were used in each case.

Time mins.	K_2O found. Grm.	K_2O found. Per cent.	Contents on cooling.
	Chemically Pure KCl.		
20	0·06383	63·83	Liquid.
30	0·06366	63·66	Syrup.
50	0·06383	63 83	Pasty.
	Chemically Pure K_2SO_4.		
20	0·05401	54·01	Liquid.
30	0·05435	54·35	Thin paste.
50	0·05467	54·67	Thick paste.

No reason can be easily assigned why the higher results were obtained on the samples when worked by the referee's directions than those given before, unless it is that the time given to the evaporation is a factor to be considered. In this connection, it might be of interest to note that in the low results obtained before, while following the referee's directions, and in some of the higher results obtained at the same time when the volume was reduced to about 5 cc. before adding the reagent, the same stock of reagent was used. Evidently, these variations were not due to the reagent, but rather to the different volumes of the solution on adding the same. In support of this, reference might be made to the more uniform results which have been obtained where this change has been made in the referee's directions.

From the above work, one must recognise that the evaporation is a point that is to be watched in the working of the method, and, in fact, an important point which needs further attention before definite conclusions can be drawn.

To determine what other factors influence the results, first the effect of precipitating in larger volumes with the reagent; second, using old nitrite reagent, and finally using more or less acetic acid was tried. Also, the plan was tried of adding the nitrite in two portions at different times in the evaporation in order to more completely precipitate the potassium by maintaining the excess of fresh reagent in the solution.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 1st, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Experiments on the Restoration of Paralysed Muscles by means of Nerve Anastomosis.*" By Robert Kennedy, M.A., M.D., D.Sc.

"*Morphology of* Trypanosoma evansi (*Steel*)." By Col. Sir David Bruce, C.B., F.R.S. (Army Medical Service).

"*Pathogenic Agent in a Case of Human Trypanosomiasis in Nyasaland.*" By Hugh S. Stannus and Dr. W. Yorke.

"*Experimental Transmission of Goitre from Man to Animals.*" By Capt. R. McCarrison.

"*Action of Radium Radiations upon some of the Main Constituents of Normal Blood.*" By Miss Helen Chambers, M.D., and S. Rust, D.Sc.

Experiments have been performed *in vitro* with the following results:—When blood is mixed with radium emanation hæmolysis occurs with gradual conversion of oxyhæmoglobin into met-hæmoglobin. The hæmolysis is a gradual process, and has been found to occur as a direct result of α radiation. Leucocytes show marked degenerative changes when exposed to α-rays. During the process of clothing leucocytes appear to move away from a region radiated by α-rays. This motion is not due to a direct action of the rays on the leucocytes, but has been attributed to changes found to occur in the surface tension of blood serum when radiated. The specific properties of opsonin and hæmolytic complement are lost when serum is exposed to α-rays. The progressive changes caused by these rays indicate the separate identity of opsonin and complement. The β- and γ-rays have yielded negative results in analogous experiments.

"*Mechanism of Carbon Assimilation.*" (Part III.). By Francis L. Usher and J. H. Priestley.

Details are given of further experiments supporting conclusions arrived at in Parts I. and II. of this series, as to the primary products of photolytic reduction of aqueous solution of carbon dioxide.

By the use of other sources of energy, viz., (i.) α- and β-rays from radium emanation and its products, and (ii.) the radiation from a quartz mercury vapour lamp, solutions of carbon dioxide have been decomposed with formation of small quantities of formaldehyde and hydrogen peroxide.

The hydrogen peroxide formed was identified by the titanium sulphate reaction; the formaldehyde by Schryver's reaction.

Further experiment with chlorophyll films are described, leading to the conclusion that bleaching of chlorophyll in sunlight, whether carbon dioxide is present or not, is due to formation of hydrogen peroxide; but the production of formaldehyde, in such condition and quantities as to be recognisable by use of Schiff's reagent, seemed only to occur when carbon dioxide was present. Evolution of oxygen, from green tissues in which the catalase has not been killed, and from gelatin films containing catalase over which a film of chlorophyll has been spread and exposed to light in an atmosphere containing carbon dioxide, has been established by further experiments.

Qualitative tests for emission of oxygen have been made by methods involving utilisation of Beijerinck's photobacteria; quantitative tests by use of apparatus enabling very small quantities of oxygen to be measured.

Further evidence that some of the energy supplied to a film of chlorophyll by sunlight is used in the photolytic reduction of carbon dioxide has been obtained by an experimental proof that such film in sunlight, in presence of carbon dioxide, is at a lower temperature than a similar film also in sunlight, but in air free from carbon dioxide.

The paper concludes with brief replies to some criticisms upon the experimental evidence and conclusions recorded in Parts I. and II. of this series of papers.

"*Contribution to our Knowledge of the Protozoa of the Soil.*" By T. Goodey.

The paper is an account of work carried out on the soil protozoa which are considered to be chiefly instrumental in limiting the activity of bacteria in the soil, and thus in helping to render the soil comparatively infertile. Methods of obtaining protozoa in cultures of soil are described, and a list of the different species found so far is given. An experimental method for quickly finding the earliest ciliated protozoa occurring in a soil culture is described, in which use is made of the galvanotactic response which many of the protozoa show when stimulated by means of a continuous electric current. By means of this method, active ciliated protozoa have been found in from one and a-half hours to four hours.

Experiments on the length of time required for a ciliated protozoon, *Colpoda cucullus*, to develop from its resting cysts have also been conducted in similar media and at the same temperature as used in the soil cultures. It has been found that the times required for development in both soil and cyst cultures are comparable, and that the first *Col. cucullus* to occur in soil cultures are almost identical in appearance with those which emerge from resting cysts.

The conclusion drawn from the experiments is that the ciliated protozoa are only present in the soil in the encysted condition, and do not therefore function as the factor limiting bacterial activity in the soil.

"*Anode and Cathode Spectra of various Gases and Vapours.*" By G. Stead.

CHEMICAL SOCIETY.

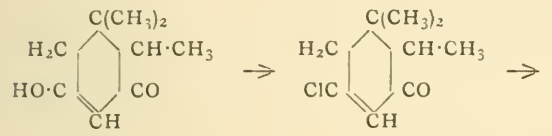
Ordinary Meeting, May 18th, 1911.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

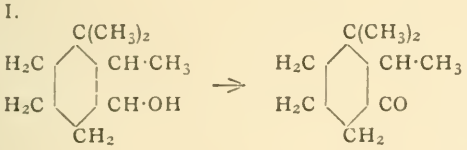
(Concluded from p. 273).

*137. "*Hydroaromatic Ketones.* Part II. 1 : 1 : 2-*Trimethyl*cyclo*hexan*-3-*one*." By Arthur William Crossley and Nora Renouf.

1 : 1 : 2-*Trimethyl*cyclo*hexan*-3-*one* (II.) has been prepared from 1 : 1 : 2-trimethyldihydroresorcin (I.) by a series of reactions indicated by the following formulæ :—

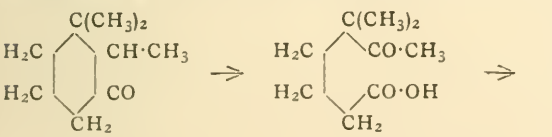


I.

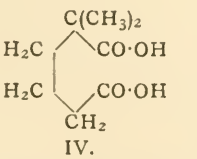


II.

The proof of the constitution of the ketone is afforded by a study of its oxidation products, which are δ-acetyl-δ-methylhexoic acid (III.) and αx-dimethylapidic acid (IV.):



III.



IV.

The preparation of the ketone was originally undertaken with the idea of comparing its properties and transformations with those of camphor, since these two substances show a marked resemblance in the arrangement of the various groupings in their molecules. During the course of the work it became evident that a closer investigation of the properties of trimethyldihydroresorcin and its derivatives was highly desirable, because the molecule is not symmetrical, as in the case of dimethyldihydroresorcin, and the work described shows that many complicated questions of isomerism are involved which are at present being more fully studied.

138. "*The Course of Chemical Change in Quinol under the Influence of Radiant Energy.*" By Walter Noel Hartley and Otway Henry Little.

For the purpose of examining the extent to which radiant energy operates on certain organic substances so as to cause a change in constitution and in chemical properties, more than thirty-six experiments were made at different temperatures, on quinol in a state of vapour, in darkness, diffused daylight, and in ultra-violet rays, flasks of glass and of quartz being used. The course of chemical change was measured by the volume of hydrogen evolved.

1. The reaction $C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + H_2$ seems to attain a condition of equilibrium when 0·6 of a mgrm.-molecule of quinol has lost 6·7 cc. of hydrogen, and the principal product is quinhydrone.

2. The reaction is not strictly reversible in the presence of air or oxygen, because under no conditions does the quinhydrone revert to quinone, except in an atmosphere of hydrogen.

3. In a flask containing crystallised quinol, quinhydrone, and *p*-benzoquinone, exposed to daylight, the *p*-benzoquinone soon disappears, its vapour reacting with the residual quinol to form quinhydrone.

4. In every instance the most complete and rapid chemical change was effected by rays of shortest wavelength.

139. "*Electrolytic Reduction.* Part IV. *Aromatic Aldehydes.*" By Herbert Drake Law.

Previous work has shown that the aromatic aldehydes, when reduced by the electrolytic method, yield resinous products in varying amount, which is least when the groups round the benzene nucleus occupy a symmetrical position. Deviations from the latter configuration influence the course of the reduction in such a manner that the resin production becomes most prominent when the change in the structure is greatest. This view has now been confirmed in the case of the three monochlorobenzaldehydes. Experiments have also been conducted in a nearly neutral medium, and this change is accompanied by a great decrease in the resin formation.

140. "*Synthesis of Ammonia by Heat.*" By Ivor Southwell Cardell and Fred Thomas.

The authors find that ammonia cannot be produced from pure hydrogen and nitrogen, but combination takes place in the presence of oxides of nitrogen.

With nitric oxide the amount of ammonia formed decreases with the increased rate of passage of the gases through the experimental tube, but the reverse holds good in the case of nitrous oxide. This is explained by the relative stability of the two oxides.

141. "*A Method of Chlorination : Chlorination of Anilines and Phenols.*" By Kennedy Joseph Previté Orton and Harold King.

The method of chlorination, which was described, is based on the reversible interaction between chloroamine and hydrochloric acid, studied by Orton and Jones (*Trans.*, 1909, xcv., 1456). By proper choice of the quantities of hydrochloric acid, any given concentration of chlorine can be obtained. This concentration will remain constant during the chlorination, since a molecule of chlorine used in substitution is replaced by a molecule of hydrogen chloride, which in its turn reacts with a further amount of chloroamine :—$Ar{\cdot}NCl{\cdot}Ac + HCl = Ar{\cdot}NH{\cdot}Ac + Cl_2$.

In this way, oxidation and other side reactions can be avoided, and the operation most effectively controlled.

A few chloro-derivatives of anilines, hitherto unrecorded, were described.

142. "*The Intermolecular Condensation of Aromatic Sulphinic Acids.* Part II. *The Interaction of Aromatic Disulphoxides and Sulphuric Acid.*" By Thomas Percy Hilditch.

The decomposition of aromatic disulphoxides by cold concentrated sulphuric acid was shown to be dependent chiefly on the number and position of the alkyl substituents in the aromatic nucleus. In all cases, however, the primary reaction can only be explained by supposing that the disulphoxide molecule undergoes hydrolytic fission with formation of a mixture of sulphinic and (unstable) sulphoxylic acids :—

$$R{\cdot}SO{\cdot}SO{\cdot}R \overset{H_2O}{\rightleftharpoons} R{\cdot}SO_2H + R{\cdot}S{\cdot}OH$$

These intermediate products may then in certain cases unite to more complex derivatives, such as oxides of the diphenylene disulphides, or, in presence of a phenolic ether, may suffer condensation to simple or complex sulphonium bases, according to the nature of the substitution in the aromatic residue.

The compounds investigated were diphenyl-, di-*p*-phenetyl-, and di-*p*-tolyl methyl ether disulphoxide, both in presence of, and without the addition of, a phenolic ether (phenetole or *p* tolyl methyl ether).

143. "*The Action of Sodium Hypophosphite on Copper Sulphate in Aqueous Solution.*" By JAMES BRIERLEY FIRTH and JAMES ECKERSLEY MYERS.

The authors have examined the above reaction in acid solution, and find that the composition of the product depends on the conditions under which the reaction is carried out. The reaction proceeds through a series of stages, and finally yields a black substance containing hydride, oxide, and phosphate of copper.

This substance, when quite dry, is unstable, and frequently decomposes spontaneously on exposure to air, with the production of water, hydrogen, copper, copper oxide, and copper phosphate.

144. "*Note on some Metallic Compounds of Substituted Ammonia.*" By WILLIAM ROBERT LANG.

In continuation of his work on the metallic compounds of substituted ammonias (Lang and Rigaut, *Trans.*, 1899, lxxv., 883; Lang, *Ibid.*, 1903 lxxxiii., 724; Lang and Carson, *Proc.*, 1903, xix., 147; Lang and Jolliffe, *Ibid.*; Lang and Carson, *Journ. Am. Chem. Soc.*, 1904, xxvi., 758; compare also Girardet, *Bull Soc. Chim.*, 1910, [iv.], vii., 1028), the author has prepared a compound from cuprous thiocyanate and trimethylamine.

Cuprous thiocyanate was carefully prepared, and subjected to the action of an excess of dry trimethylamine, the reaction vessel—similar to that employed in former experiments—being cooled by solid carbon dioxide. After remaining in contact with the copper salt for several days, the excess of methylamine was removed, and the resulting compound examined. A second and third application of trimethylamine, with subsequent drying and weighing, yielded the same result, namely, a compound corresponding with the formula $CuSCN.N(CH_3)_3$.

145. "*The Decomposition of Diethylenesulphidemethylsulphine Hydroxide in Aqueous Solution.*" By LEILA GREEN and BRENDA SUTHERLAND.

The hydroxide corresponding with the salts of diethylenesulphidemethylsulphine decomposes spontaneously into water and a neutral oil (Masson, *Trans.*, 1886, xlix., 233; Mansfeld, *Ber.*, 1886, xix., 696, 2658; V. Meyer, *Ibid.*, 3262). The authors have measured the velocity of this action at 55° in solutions sufficiently dilute to justify the simplifying assumption of total ionisation, using solutions of the pure hydroxide, and also others containing excess of hydroxyl (added sodium hydroxide), or of the sulphine cation (added $C_5H_{11}S_2I$). The results show that the action is of the second order, and that the velocity is directly proportional to the concentration of each of the ions of the sulphine base; or it may be represented by the equation: $-C_5H_{11}S_2^{\cdot} + OH' = C_5H_{10}S_2 + H_2O$.

146. "*Properties of Binary Mixtures of some Liquefied Gases.*" By LANCELOT SALISBURY BAGSTER.

In a previous paper (*Trans.*, 1910, xcvii., 2607) an account was given by the author, in conjunction with Dr. B. D. Steele, of the vapour-pressure curves of binary mixtures of hydrogen sulphide with hydrogen bromide and hydrogen iodide. Hydrogen bromide gave a curve with a minimum, hydrogen iodide a straight line. The freezing-point curves of the above mixtures have been determined in order to ascertain whether there was a corresponding difference. Both curves are of the same type. They are continuous, showing a minimum, but no eutectic-point, being of the form produced by a system in which the solid phase consists of mixed crystals. Thus the difference indicated by the vapour-pressure curves is not borne out by the freezing-points.

147. "*Note on the Monosodium Salt of 1-Nitroso-2-naphthol 3 : 6 disulphonic Acid.*" By PERCY MAY.

The aqueous solution of the monosodium salt of 1-nitroso-2-naphthol-3 : 6-disulphonic acid, $NO\,C_{10}H_4(OH)(SO_3H)\cdot SO_3Na,\frac{1}{2}H_2O$, is orange-red, becoming pink on dilution. Solutions of the neutral salts are dark green, turning to yellowish green on dilution.

148. "*Synthesis of Pinacones.*" (Part I.). By WILLIAM PARRY.

By the action of the appropriate Grignard reagent on ethyl α-hydroxy*iso*butyrate (*Proc.*, 1909, xxv., 305), the following pinacones have been prepared:—

1. Pinacone, which was isolated in the form of its hydrate, $OH\cdot CMe_2\cdot CMe_2\,OH.6H_2O$, melting at 44—46°.

2. *β-Methyl γ-ethylpentane-βγ diol* $OH\,CMe_2\,CEt_2\,OH$; a colourless viscid oil boiling at 100°/20 mm., soluble in boiling water. Repeated fractionation under atmospheric pressure results in the elimination of the elements of water with the production of *diethylisopropenylcarbinol*, $CH_2{:}CMe\cdot CEt_2\,OH$, which has an odour of camphor, and boils at 150—152°/767 mm.

3. *β-Methyl-γ-propylhexane-βγ-diol*, $OH\cdot CMe_2\,CPr^{\alpha}_2\cdot OH$; a colourless viscid oil, boiling at 105°/15 mm. It cannot be distilled under the ordinary pressure without losing the elements of water.

4. *αα-Diphenyl-β-methylpropane-αβ-diol*,—

$$OH\cdot CMe_2\cdot CPh_2\,OH;$$

white silky needles, melting at 89—89·5°, and readily soluble in the common organic media, with the exception of light petroleum. Acetic anhydride containing one or two drops of sulphuric acid dehydrates it, with the formation, probably, of as-*diphenyldimethyl ethylene oxide*, $\begin{matrix}CMe_2\\|\\CPh_2\end{matrix}\!\!>\!O$, colourless prisms, melting at 44—45°.

5. *αα-Dibenzyl-β-methylpropane α -diol*,—

$$OH\,CMe_2\,C(CH_2Ph)_2OH;$$

colourless prisms, melting at 47—48°. At the same time a small quantity of an unsaturated alcohol is formed, which distils at 165—168°/12 mm. and is probably *dibenzylisopropenylcarbinol*. $CH_2{:}CMe\cdot C(CH_2Ph)_2\,OH$.

6. *αα-Dinaphthyl β-methylpropane-αβ-diol*, $OH\,CMe_2\cdot C(C_{10}H_7)_2\cdot OH$; small white crystals, melting at 166—166·5°.

The solid pinacones have normal molecular weight in dilute benzene solution.

Experiments are now being conducted with ethyl α-ethyl-α-hydroxybutyrate, which appears to react in a different manner with the magnesium alkyl haloids.

149. "*A Method for the Accurate Estimation of Traces of Water in Ether.*" By DAN TYRER.

It is occasionally of importance to determine with accuracy the amount of water contained in a sample of "wet" ether. A method susceptible of a great degree of accuracy can be based on the fact that the addition of a little water to ether greatly increases its solvent power for some solutes. The most suitable substance which can be used as a solute is cadmium iodide. According to Eder (*Dingl. Polytech. Journ.*, 1876, ccxxi., 189), cadmium iodide is soluble in "absolute" ether to the extent of 28 per cent. Using a very dry sample of ether, it was found by the author, however, that cadmium iodide is practically insoluble in ether. It is to be presumed that the high value obtained by Eder was due to the ether he used containing water and alcohol. In the following table is given the solubility of cadmium iodide at 12° in pure ether, and in ether containing various quantities of water. The ether used was Kahlbaum's pure material, prepared from ethyl alcohol, and thoroughly dried by twice distilling over phosphoric oxide.

Grms. of water in 100 of ether.	Grms. CdI_2 per 100 of solvent.
0·0	0·143
0·10	0·78
0·30	2·07
0·50	3·36
0·70	4·77
0·90	6·46
1·00	7·30
1·10	8·27
1·14 (saturated)	8·68

The above results were read from a smoothed curve of experimental values. On inspecting the table it will be seen that an addition of 0·1 per cent of water to dry ether increases the solubility of the cadmium iodide by about 0·64 unit. Now as the solubility can be determined with ease to within an error less than 0·1 unit, the percentage amount of water in the ether can be found to less than 0·001 unit.

This method of analysis might be extended to the determination of traces of water in the alcohols, it being only necessary to find a suitable solute and to obtain a perfectly anhydrous alcohol.

150. "*Equilibrium in the System: Ethyl Alcohol, Acetic Acid, Ethyl Acetate, and Water, and its apparent Displacement by Hydrogen Chloride.*" By William Jacob Jones and Arthur Lapworth.

The authors find that the equilibrium constant in this liquid system appears to rise from the usually accepted value 4, to at least 8, when hydrogen chloride is present in considerable quantities. No ethyl chloride was formed during the experiments, the whole of the hydrogen chloride being recovered.

The observations are easily accounted for on the assumption that the hydrogen chloride unites with part of the water, and the numbers obtained at 25° suggest that one molecule of hydrogen chloride removes two molecules of water from the sphere of action.

151. "*The Heat of Hydrolysis of Ethyl Alcohol Hydrochloride.*" (A Correction). By William Jacob Jones and Arthur Lapworth.

An arithmetical blunder led the authors to record the heat associated with the reaction:—

$$C_2H_6O,HCl + H_2O = C_2H_6O + H_2O,HCl,$$

or, more strictly:—

$$C_2H_6O,H^{\cdot} + H_2O = C_2H_6O + H_2O,H^{\cdot},$$

in alcoholic solution, as, roughly, 1100 grm.-calories. The true value is much greater than this, probably about 4300 grm.-calories (compare *Proc. Chem. Soc.*, xxvii, 101).

152. "*Derivatives of Silicoethane and Silicoethylene.*" By Frederic Stanley Kipping.

For some time past the author has been making experiments on the linking together of silicon atoms, and in the course of this work he has studied the action of sodium on various aryl and alkyl-aryl-substitution products of silicon tetrachloride. The investigation is still incomplete, but a preliminary note on the subject seems to be desirable in view of Schlenk, Renning, and Racky's paper on hexaphenylsilicoethane, which has just been published (*Ber.*, 1911, xliv., 1178).

Hexaphenylsilicoethane, $SiPh_3 SiPh_3$, was prepared from triphenylsilicyl chloride by the author more than a year ago; it crystallises well from tetrachloroethane, and melts at about 360°.

The compounds obtained from the disubstitution products of silicon tetrachloride have properties very different from those of this saturated substance; from phenylethylsilicon dichloride, for example, a compound having the composition of *diphenyldiethylsilicoethylene*, SiPhEt:SiPhEt, is easily produced, but it is a vitreous and easily fusible solid, readily soluble in most of the common solvents, except the alcohols.

NOTICES OF BOOKS.

A Class book of Chemistry. By G. C Donington. M.A. London: Macmillan and Co., Ltd. 1911. (3s. 6d.).

This book is the outcome of the author's experience of the difficulty of teaching chemistry in such a way as to develop the pupils' observational, reflective, and deductive powers, while at the same time giving them a sound knowledge of the most important facts and theories which should be thoroughly familiar to all students of elementary chemistry before they proceed to more advanced work. The book covers the syllabus of the Board of Education, London Matriculation, and other examinations, and contains reprints of typical examination papers, as well as a graduated series of tests on the text and well chosen questions on the subject of each chapter. Additional problems are provided to occupy the spare time of the quicker and more able pupils, and the experiments are described in the text fully enough to minimise the explanatory and supervisional work of the demonstrator. The book will be a boon to teachers in charge of large classes, especially those who realise that the exclusive adoption of the research method in teaching chemistry leads to results which are not altogether satisfactory even in the case of the best students.

Lectures on Iron Founding. By Thomas Turner. M.Sc., A.R.S.M., F.I.C. Second Edition. London: Charles Griffin and Co., Ltd. 1911. (3s. 6d. net).

This book on Iron Founding is an extension of a series of lectures on cast-iron which were given under the auspices of the School of Metallurgy of the University of Birmingham. In these lectures, which were intended for, and attended by, men actually engaged in iron founding as well as the students of the University, the materials employed in iron founding, the constituents of different irons, as well as the general plant employed, were thoroughly discussed by the lecturer, and special attention was paid to any difficulties which are likely to occur, *e.g.*, the occurrence of shut ends, rough surfaces, sponginess, &c., and their causes and remedies and the economics of the subject was not neglected. In the new edition some fresh matter has been added dealing more particularly with recent physico-chemical work and with changes occurring during the solidification of cast-iron, and some of the original illustrations have been replaced by better ones.

Rubber. By Clayton Beadle and H. P. Stevens, M.A., Ph.D., F.I.C. London, Bath, and New York: Sir Isaac Pitman and Sons, Ltd. (1s. 6d. net).

The general reader who wishes to know something of rubber and the manufacture of rubber articles will find that this book gives him in a pleasant easy style an interesting and clear account of the subject. In it are described the processes employed in obtaining the raw material, its preparation for use in the industries and arts, and methods of making the chief classes of rubber goods, tyres, washers, mackintoshes, &c. The manufacturer may thus learn from it something of the methods of the planter, and after reading it the latter may understand better the requirements of the manufacturer, and the book, which lays claim to be no more than an introduction to the study of rubber may be said to answer satisfactorily to this description.

A Concise History of Chemistry. By T. P. Hilditch, B.Sc. (Lond.), A.I.C. London: Methuen and Co., Ltd. 1911. (2s. 6d.).

This book would probably be of more use to teachers than to general students, although candidates for examinations might find that its succinctness and the order in which the matter is presented would be special recommendations. The subjects are taken up as a rule in the order in which the student would meet with them in a general text-book

or in a course of lectures. Thus the early chapters deal with the history of the investigation of the air, of water, the ultimate constituents of matter and inorganic compounds, and include a chapter of notes on the history of the elements. Then organic chemistry, biochemistry, applied chemistry, and finally physical chemistry are considered. The teacher will find in each chapter a useful *résumé* of the historical facts which throw light upon the development of our knowledge, and will greatly appreciate the appendices, one of which gives a biographical index of chemists with brief notes on their work, while the second is a complete chronological survey of the chief events of chemical interest from 1660—1909, including discoveries and the formulation of theories.

CORRESPONDENCE.

REDUCTION OF SILVER CHLORIDE.

To the Editor of the Chemical News.

SIR,—In the laboratory it is often required to make small quantities of silver nitrate from a silver coin, or from a small accumulation of silver chloride. The method of reducing the silver chloride by fusing with sodium carbonate in a fire-clay pot is long and inconvenient; the method of reduction by contact with zinc is also tedious, and, moreover, is often rendered unsuitable for analytical work owing to impurities in the zinc. The best laboratory method would then seem to be the well known one of reduction by boiling with sugar and potassium hydrate. This, however, is also at fault, owing to the fact that the first portion of metallic silver produced forms a protective coating around the unaltered silver chloride, thus preventing complete reduction. It was thought that this difficulty in the last method could be entirely obviated, or at least minimised, by first dissolving the silver chloride in ammonium hydrate, before boiling with the sugar and potassium hydrate.

This idea was tested, and was found to work so well in practice that the filtrate from the reduced silver was entirely free from the metal, and, moreover, after thoroughly washing the reduced silver with hot water, the metal dissolved completely in dilute nitric acid, leaving no trace of silver chloride. The reduced silver formed a non-adherent mirror on the sides of the vessel, which broke into a more or less spongy mass on continued boiling. The above idea led to another method of reduction to metallic silver.

Remembering that hydrogen peroxide reduces silver oxide to metallic silver, it was thought probable that the addition of sodium peroxide to a cold ammonia solution of silver chloride would lead more conveniently to the same result. This was found to be the case when actually tried, and no silver could be detected in the filtrate, provided a sufficiency of sodium peroxide were used. Instead of adding the peroxide to the solution, it was found to be a saving of the former if the solution were poured gradually on it, less peroxide being required for a given quantity of solution.

When action had apparently ceased, the mixture was boiled, diluted, and filtered. The silver formed by this method also dissolved completely in dilute nitric acid, being free from all traces of the chloride.

These suggestions are put forward as quick and convenient methods of converting small quantities of silver chloride into metallic silver, from which the nitrate may be obtained.

Whilst no claim is laid to this being novel, I have seen no previous mention of these methods, so they may be found useful.—I am, &c.,

EDGAR H. BOOTH.

Sydney University, Australia,
May 8, 1911.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 14, April 3, 1911.

Formula of Uranium Carbide.—Paul Lebeau.—The analysis and the metallographical examination of melts of uranium containing carbon show that the carbide of uranium existing in graphitic melts has the formula C_2Ur. Both in formula and properties this compound resembles the carbides of the rare earths. As regards the complexity of its products of decomposition with water it is most like thorium carbide.

Mercuric Oxychlorides.—M. Driot.—The mercuric oxychloride formed in the dry way has the formula $HgCl_2.2HgO$. When a boiling solution of sublimate is saturated with mercuric oxide from solutions containing small amounts of sublimate (0·5—4 per cent) fine needles of formula $HgCl_2.3HgO$ are obtained. 4—8 per cent solutions give $HgCl_2.2HgO$, while 13 per cent solutions give $2HgCl_2.HgO$. A 30 per cent solution at 100°, after treatment for five or six days with finely powdered oxide, gives the compound $HgCl_2.HgO$.

Formation of Ethyl Chlorethoxyacetate.—E. E. Blaise and L. Picard.—Ethyl chlorethoxyacetate cannot be prepared by the direct chlorination of ethoxyacetic ether, but it may be obtained by replacing the hydroxyl of the alcoholate of ethyl glyoxalate by chlorine. The transformation can be effected by means of thionyl chloride at 75—80°. In this reaction the ethoxy group must change places with the chlorine :—

$$(C_2H_5{-}O)_2CH{-}CO_2H \rightarrow (C_2H_5{-}O)_2CH{-}COCl \rightarrow (C_2H_5O)CHCl{-}CO_2C_2H_5.$$

The condensation of zinc alkyls with chlorethoxyacetic ether to give α-ethoxy acids is interesting, in that it constitutes a method of synthesising the α-acid alcohols by the fixation of the group $-CHOH-CO_2H$ to any carbon radical whatever.

New Series of Leuco-bases and Dyes from Diphenylethylene.—P. Lemoult.—By the action of Michler's ketone on alcoholic magnesium iodide derivatives ethylenic compounds of the two types—

$$\text{I. } \begin{matrix} H \\ R \end{matrix}\!\!>\!C{=}C{-}C_6H_4N(CH_3)_2,$$

$$\text{II. } \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!C{=}C{-}C_6H_4N(CH_3)_2$$

are obtained. When nitrous acid is used as a transformation agent the compounds of type I. give true dyes and are true leuco-bases, while those of type II. give only very feeble dyes and are pseudo-leuco-bases. Ethylenic hydrogen is indispensable.

Smoke Utilisation and Prevention.—A Liverpool Demonstration.—Especially at a time when there is talk of garden cities and the improvement of the amenities of life does the question of smoke consumption bulk largely in the public mind. It is a problem that has engaged the attention of many inventors, amongst others the Salamander Fire Bar and Smoke Preventor Co., Ltd., of Liverpool. For the method devised by this Company it is claimed that not only can the issue of black gaseous smoke be prevented in a very simple manner, but that what is produced can be converted into heat, thus effecting a saving of fuel and other economies of vast importance to manufacturing industries. As a practical demonstration the Company invite an inspection of premises at 41, Stanhope Street, Liverpool, where steam has to be maintained, yet not a vestige of smoke is seen all day long.

THE CHEMICAL NEWS.

Vol. CIII., No. 2691.

THE OCCURRENCE OF SULPHATES IN RIVER-WATERS.*

By R. B. DOLE.

In Chemical News for August 12, 1910 (vol. cii., p. 75), Mr. H. S. Shelton presented an article on the correlation of rock and river-water analyses. Besides other comments on the information now available on that subject, Mr. Shelton draws attention to an alleged discrepancy between the percentage of sulphur in rocks and the percentage of sulphates found by analysts in the waters of streams, and he concludes that a considerable proportion of so-called sulphate in river-waters is not sulphate at all, but some other substance or substances that form barium salts not soluble in hydrochloric acid. As the reliability of an enormous mass of analytical data is thus laid open to suspicion, the comment should not pass unchallenged. The object of this brief note is to demonstrate that in the United States, and therefore probably in other parts of the earth's land surface, many river-waters carry in solution large quantities of sulphur in the form of sulphates.

It may be noted in passing that Sir John Murray's average of the substances in solution in the rivers of the world differs considerably from the average by Dr. F. W. Clarke, which was computed from more data. The later figures indicate the presence of even more chlorides and sulphates than Murray calculated. The two estimates are compared :—

Average Composition of the Inorganic Matter in Rivers of the World.

	Murray (*a*).	Clarke (*b*).
Silica, SiO_2	10·75	11·67
Oxides of iron and aluminium, $Fe_2O_3 + Al_2O_3$	4·76	2·75
Calcium, Ca	20·46	20·39
Magnesium, Mg	4·65	3·41
Sodium, Na	3·47	6·40
Potassium, K	1·33	1·51
Carbonate radicle, CO_3	41·33	35·15
Sulphate radicle, SO_4	8·22	12·14
Nitrate radicle, NO_3	2·82	0·90
Chlorine, Cl	1·85	5·68
Minor constituents	0·36	—
	100·00	100·00

(*a*) *Scottish Geol. Mag.*, 1887, iii., 65; quoted in Clarke's "Data of Geochemistry," *Bull. U.S. Geol. Survey*, 1908, No. 330, p. 88, in revised form.

(*b*) F. W. Clarke, "A Preliminary Study of Chemical Denudation," Smithsonian Miscellaneous Collections, June, 1910, vol. lvi., No. 5, Washington. Minor constituents are disregarded in computing the average.

Since 1904 chemists of the Water Resources Branch of the United States Geological Survey have systematically studied the quality of surface waters. Though the analyses have been made primarily to discover the industrial values of the waters, the estimates of inorganic constituents are applicable to discussions of erosion and denudation. Samples of water have been collected daily for a year at more than 200 stations on the principal rivers of the country. (The analytical procedures and many of the analyses have already been published; see "Water-supply Papers," U.S. Geol. Survey, Nos. 236, 237, and 239; Nos. 273 and 274 are in press). The daily samples have been united in sets of ten, and the principal inorganic constituents of the composites thus obtained have been determined. The analytical work has been performed by more than thirty chemists in ten laboratories.

The method uniformly and consistently followed in reference to sulphates is outlined. The filtered water was evaporated to dryness, invariably in platinum on a water-bath, and the residue was dried at 180° C. for one hour, being subsequently carbonised if much organic matter was present. The silica was then dehydrated by evaporation with hydrochloric acid, and filtered from the acid solution. Iron and aluminium were removed by precipitation with ammonium hydrate, after which the filtrate was slightly acidulated with hydrochloric acid, and was heated nearly to boiling. After excess of barium chloride in hot 10 per cent solution had been added, the liquid was digested on a hot plate for at least thirty minutes. The precipitate was removed by filtration, thoroughly washed with hot water, dried, ignited, and weighed. The amount of sulphates as parts per million of SO_4 was computed from that weight. This treatment certainly precludes great error by retention of silicates or organic compounds in the precipitate. The amount of river-water represented in the weighed precipitate was usually 250 cc., but if sulphates were very low 500 or 1000 cc. were taken, and 1500 to 4000 cc. were used in testing water from Androscoggin River, at Brunswick, Maine, and Mississippi River, at New Orleans, Louisiana. It is hardly necessary to add that only carefully tested reagents were used in the analyses. Particular attention may be directed to the fact that the precipitation in the procedure just outlined was not made in the raw water itself, as suggested by J. A. Wanklyn ("Water Analysis," 1896, 10th ed., p. 111), to whom Shelton refers, and by Tieman and Gartner ("Handbuch der Wasser," 1895, 4th ed., p. 216), but in an acid solution of the residue after removal of silica, iron, and aluminium. This is the gravimetric method described by C. R. Fresenius ("Quantitative Chemical Analysis," 1904, Trans. 6th German ed., i., 434). Though W. F. Hillebrand ("The Analysis of Silicate and Carbonate Rocks," *Bull. U.S. Geol. Survey*, 1910, No. 422, p. 193) and other chemists have investigated numerous errors to which it is subject, none has attributed to it the absolutely gross unreliability that Shelton's comment insinuates.

Even if it were insisted that determinations of small amounts of sulphates are erroneous, nevertheless it can only be admitted that many surface waters representing the discharge from extensive areas contain amounts of sulphates so large that great errors in their estimation are highly improbable. Only a few analyses of such waters are quoted here, but they are sufficiently numerous to be significant. It should be emphasised that the figures given are not dependent on miscellaneous analyses, but are computed from examinations of systematically collected samples representing the average condition for not less than one year.

Sulphates in the Water of some American Rivers,

	Drainage area (square miles).	Water taken for estimate. Cc.	Sulphate radicle, SO_4. Parts per million.	Sulphate radicle, SO_4. Anhydrous residue. Per cent.
A.	32,300	250	279	25·5
B.	15,100	250	144	31·4
C.	528,000	250	104	30·6
D.	56,900	100—250	140	25·7
F.	235,000	250	228	30·1
	867,300			

A. Brazos River, near Waco, Texas; analyses by W. M. Barr, Walton Van Winkle, Chase Palmer, W. D. Collins, and R. B. Dole.

B. Minnesota River, at Shakopee, Minnesota; analyses by same.

* Published by permission of the Director, United States Geological Survey.

C. Missouri River, at Ruegg, Missouri; analyses by same.

D. Red River, at Shreveport, Louisiana; analyses by J. R. Evans, Chase Palmer, W. D. Collins, and R. B. Dole.

F. Rio Grand, at Laredo, Texas; analyses by C. H. Stone, P. L. McCreary, and F. M. Eaton.

Each of these rivers, which drain a total area of nearly 870,000 square miles, carries more than 100 parts per million of sulphates, equivalent to over 25 per cent of the inorganic matter in solution and representing usually weighed amounts of over 60 mgrms. $BaSO_4$. If Colorado River and some other streams of western United States were included the area shown to yield highly sulphated waters would be more than doubled. These five rivers lie west of Mississippi River, two of them discharging into it, and they traverse regions of easily disintegrated, lately deposited limestones and sandstones high in readily soluble material. Though eastern tributaries of Mississippi River, draining regions where the older, harder, less readily soluble limestones and sandstones predominate, are not so high in sulphates as the five waters just mentioned, nevertheless they contain notable amounts of that radicle, and the effect of it is reflected in the main stream. The anhydrous residue from water of Mississippi River, at Minneapolis, Minnesota, contains 9·3 per cent of SO_4; at Moline, Illinois, 13·6 per cent; near Chester, Illinois, 21·8 per cent; at Memphis, Tennessee, 20·6 per cent; and at New Orleans, Louisiana, 15·4 per cent (drainage area, 1,265,000 square miles).

The large mass of analytical evidence now at hand makes it clear that sulphates occur in both surface and underground waters entirely out of proportion to the percentage of sulphur computed for igneous rocks, shales, sandstones, and limestones. It is not proper to discuss that relation here, but some phases of it may be mentioned. In comparing the relative amounts of the substances in rocks and in waters, due weight should be given to the fact that aqueous solutions represent the more readily soluble constituents, and not all the constituents in regular proportion. It is obvious that drainage waters contain elements not simply in proportion to the occurrence of these elements in the rocks from which the waters come, but in proportion to the solubility of the different chemical compounds in the rock complex. Part of a given rock goes into solution at once, part goes into solution very slowly, and part never is dissolved at all, but is carried to the ocean as suspended matter.

Conditions in the drainage basin of Youghiogheny River, from which samples were collected at McKeesport, Pennsylvania, illustrate this point excellently, and they demonstrate at the same time that pyrite and other sulphur-bearing minerals cannot be summarily disregarded as sources of sulphates in water. Youghiogheny River, with an area of 1770 square miles above the sampling station, receives drainage from bituminous coal deposits and piles of culm, or mine waste. The river-water ranged in a year from an alkalinity equivalent to 7·5 parts per million HCO_3 during high-water periods to an acidity equivalent to 75 parts per million of H_2SO_4 during low-water periods. Its average content of sulphates is 123 parts per million, equivalent to 68·0 per cent of the anhydrous residue. The source of these sulphates has been shown by Leighton to be the sulphur compounds of the coal beds ("Water-supply Paper," U.S. Geol. Survey, No. 108, p. 24). Oxidation of the sulphur produces a substance whose solubility is so high in comparison with the other constituents of the mine wastes that it becomes the principal ingredient of the drainage, while other substances occurring in enormously greater proportion in the rocks are either left behind or are not dissolved but are carried away in suspension.

Throughout Mississippi Basin ground waters, which contribute a large part of the surface flow, contain notable amounts of sulphates and chlorides. The following averages prepared by the writer show the character of the effluent from old limestones and unconsolidated material, largely derived from the disintegration of limestones, sandstones, and shales in Indiana and Ohio.

Average Composition of certain Ground Waters.

	Per cent of anhydrous residue.			
	A.	B.	C.	D.
Silica, SiO_2	4·1	4·4	4	4
Ferric oxide, Fe_2O_3	0·3	0·4	0	0
Calcium, Ca	20·9	19·6	18	18
Magnesium, Mg	7·1	7·4	6	9
Sodium and potassium, Na + K	4·1	6·5	6	5
Carbonate radicle, CO_3	34·6	40·2	38	40
Sulphate radicle, SO_4	17·5	16·8	17	18
Nitrate radicle, NO_3	0·6	0·2	0	0
Chlorine, Cl	10·8	4·5	11	6
Salinity (parts per million)	436	418	530	440

A. Average of 169 analyses of water from the unconsolidated deposits of north-central Indiana ("Water-supply Paper," U.S. Geol. Survey, No. 254, pp. 260 and 261).

B. Average of 83 analyses of water from the fresh water limestones of north-central Indiana ("Water-supply Paper," U.S. Geol. Survey, No. 254, pp. 260 and 261).

C. Average of 120 analyses of water from the unconsolidated deposits of south-western Ohio ("Water-supply Paper," U.S. Geol. Survey, No. 256).

D. Average of 20 analyses of water from the "Niagara" limestone in south-western Ohio ("Water-supply Paper," U.S. Geol. Survey, No. 256).

Carbonates are, of course, predominant among the acid radicles in these waters, but sulphates amount to 17 or 18 per cent of the residues, and chlorine ranges from 5 per cent in the waters of the limestones to 11 per cent in the waters of the drift, till, and alluvium. Sedimentary rocks in the United States, so far as is known by the writer, consistently yield waters containing much higher percentages of sulphates and chlorides than do the igneous and crystalline rocks. This is what might be anticipated if it is assumed that the rocks furnish all the mineral constituents of their effluent waters, after allowing for cyclic salt and for carbon dioxide derived from rain and vegetation. Hydration, oxidation, and mechanical disintegration during metamorphosis make the rock constituents less resistent to the action of water, and therefore the later formations may be expected to yield waters containing the highest proportion of the more easily soluble constituents.

It is possible that the amount of sulphates and chlorides capable of being furnished by unlocated and possibly impure deposits of gypsum, salt, and residual liquors has been under-estimated. The effect of such deposits is not negligible but is considerable, as has been pointed out, by means of analyses of water from the chain of Great Lakes between the United States and Canada (R. B. Dole, "The Waters of the Great Lakes," *Journ. New England Water Works Assoc.*, 1909, xxiii., 254).

Average Chemical Composition of Water from Two of the Great Lakes.

	Per cent of anhydrous residue.	
	Lake Superior.	Lake Erie.
Silica, SiO_2	12·7	4·5
Calcium, Ca	22·4	23·4
Magnesium, Mg	5·3	5·7
Sodium and potassium, Na + K	5·5	4·9
Carbonate radicle, CO_3	47·5	44·8
Sulphate radicle, SO_4	3·6	9·8
Nitrate radicle, NO_3	0·9	0·2
Chlorine, Cl	1·9	6·6
Ferric oxide, Fe_2O_3	0·2	0·1
Salinity (parts per million)	58	131

Lake Superior is surrounded by igneous and crystalline rocks, granite, schist, gneiss, and basalt occurring in great abundance. This accounts for the low salinity of its water. Lake Erie, on the other hand, is affected by the limestones and sandstones of the sedimentary series, and, as a result, its mineral content is more than doubled. The unquestionable increases in the percentage of sulphates and chlorine can be logically explained by attributing them to drainage from the well known salt deposits in the basin and to others yet undiscovered. Though Lake Erie is nearer than Lake Superior to Atlantic Ocean, Jackson's normal chlorine work in New York and New England shows how inappreciable is the effect of wind-borne salt on the water of either lake ("The Normal Distribution of Chlorine," "Water-supply Paper," U.S. Geol. Survey, 1905, No. 144).

It has not been the intention of the writer to review seriatim Mr. Shelton's paragraphs, though several more of his comments and conclusions are open to severe criticism. His contention that sulphates are grossly overestimated, however, demands complete refutation by analytical chemists, and it is believed that enough analytical data have been presented to demonstrate how ill-founded his objection is. Though the source and the ultimate disposal of sulphates in river waters may be obscure to the casual observer, the presence of that radicle in appreciable amount is indisputable. The work that is now being done by the United States Geological Survey on the mineral content of American rivers has established that point beyond reasonable question, and it has fully corroborated the results of other analysts who have made any extended studies of the composition of surface waters.

VOLUMETRIC DETERMINATION OF POTASSIUM BY THE COBALTI-NITRITE METHOD.*

By O. M. SHEDD.

(Concluded from p. 284).

Effect of Volume.—Ten cc. of new nitrite reagent were added to 0·10 grm. of the sample in the volume indicated, which included the volume of the reagent added. The evaporations were then made in the usual manner. In the case of KCl, the residue after evaporation consisted mostly of the greenish substance already mentioned, and only a small amount of the potassium salt.

Chemically Pure KCl.

Volume including reagent (cc.).	K_2O found (grm.).	K_2O found (per cent).
200	0·00377	3·77

A. O. A. C. Muriate.

100	0·03533	35·33

To illustrate further what effect the reducing of the volume of the solution before adding the reagent has on the results obtained, those determinations made on the A. O. A. C. muriate according to the referee's directions, and also where the volume was further concentrated to 5 cc. before adding the reagent, are given for comparison (see Table, next column).

The plan was also tried of adding the nitrite reagent to the dry residue of the salt after evaporation, but on account of the potassium salt being precipitated so finely divided that it was impossible to filter it, the determination was discarded. This was repeated with the same result.

Effect of Old Reagent.—The reagent used here had been made for about eight months, and kept in the dark. The referee's directions were followed in the work, except in the last two determinations on the muriate. In these the volume of the solution was about 5 cc. on adding the reagent.

Volume of solution on adding reagent (cc.)	K_2O found (grm.).	K_2O found (per cent).
25	0·04928	49·28
25	0·05022	50·22
25	0·05125	51·25
25	0·05187	51·87
25	0·05226	52·26
25	0·05179	51·79
25	0·05145	51·45
25	0·05145	51·45
25	0·05136	51·36
25	0·05104	51·04
25	0·05159	51·59
25	0·05119	51·19
25	0·05110	51·10
	Average	51·22
5	0·05159	51·59
5	0·05151	51·51
5	0·05223	52·23
5	0·05155	51·55
5	0·05169	51·69
5	0·05142	51·42
5	0·05142	51·42
5	0·05159	51·59
5	0·05134	51·34
5	0·05095	50·95
5	0·05108	51·08
	Average	51·49

A. O. A. C. Muriate.

Reagent used. Cc.	K_2O found. Grm.	K_2O found. Per cent.	Contents on cooling.
10	0·03531	35·31	Dry.
10	0·03655	36·55	Dry.
20	0·05050	50·50	Dry.
20	0·05076	50·76	Dry.
	Kainit.		
20	0·06085	12·17	Dry.
20	0·06095	12·19	Dry.

In connection with the above work, the following experiments were tried to see if it was possible to determine colorimetrically how much the old reagent had decomposed on standing. Two cc. each of the new and of the old reagents were diluted to 50 cc. in Nessler tubes, and, by comparing the two, it was found that, judging from the colour, two-fifths of the old reagent had decomposed.

When the colour test was made on the old reagent in the above, the solution had the characteristic brown colour of the reagent. After the test was made, the tubes were left standing in the light for about six hours, and during that time about one hour in the sunlight. At the end of the time, the solution in the tube containing the old reagent had changed to pink, showing complete decomposition, while the new reagent solution was still faint brown, but much lighter in colour than before, showing a decided decomposition had taken place. After standing about one and a-half hours longer in the sunlight, this solution also became pink in colour.

Evidently the reagent must be kept in the dark to prevent decomposition.

Effect of more or less Acetic Acid.—The plan followed was to evaporate the solution to about 5 cc. volume, 15 cc. new reagent added, and the amounts of acetic acid stated. The contents of the dishes were evaporated until the volume was about 5 cc., when they were taken from the bath. This was done in order to eliminate any error caused by further evaporation.

* *Journal of Industrial and Engineering Chemistry*, ii., No. 9.

A. O. A. C. Muriate.

Acetic acid. Cc	K_2O found. Grm.	K_2O found Per cent.	Content on cooling
None	0·05142	51·42	Thin paste.
1	0·05134	51·34	Thin paste.
5	0·05246	52·46	Pasty.

A. O. A. C. Kainit.

None	0·06330	12·66	Thin paste.
1	0·06315	12·63	Thin paste.
5	0·06450	12·90	Pasty.

Addition of the Reagent in Two Portions.—The determinations below were made according to the referee's directions; that is, by adding 10 cc. new reagent to the volume at 25 cc. The solution was then evaporated to about 5 cc. volume and 5 cc. more of reagent were added. The evaporation was continued until the contents were dry on cooling.

Muriate.. .. .. 50·09 per cent K_2O
Kainit .. .. .. 12·41 per cent K_2O

In the following experiments an attempt was made to estimate the potassium by adding the salts which compose the nitrite reagent in separate solutions at the time the evaporation was to be made. In other words, it simply consisted of preparing the reagent in the presence of the potassium salt to be estimated. If found to work, it was thought that this would improve the method, because it would be possible in this way to regulate the volume of the solution, which is important, and at the same time avoid the use of the prepared reagent which decomposes slowly on standing.

For the work 220 grms. $NaNO_2$ were dissolved in H_2O, and made to 500 cc., and designated the sodium nitrite solution. 113 grms. of cobalt acetate were dissolved in H_2O and 100 cc. 50 per cent acetic acid added (one-half of the amount prescribed), and the solution made to 500 cc. and designated as the acetate solution.

A. O. A. C. Muriate.—The solution containing 0·10 grm. salt was evaporated to dryness, and taken up with 5 cc. of the sodium nitrite solution, and then 5 cc. of the acetate solution were added, but no acetic acid, and the whole evaporated until the contents were pasty on cooling. Result, 50·59 per cent K_2O.

Another trial was made in the same manner, except the acetate solution was added first and then the sodium nitrite. Result, 51·53 per cent K_2O.

Chemically Pure K_2SO_4.—The same method as followed in the second determination above was then tried on a solution containing 0·10 grm. of the salt, and the evaporation continued until the contents were dry on cooling. Result, 52·43 per cent K_2O.

Some further determinations were made on 0·10 grm. aliquots of chemically pure K_2SO_4 and chemically pure KCl by adding the acetate to the dry residue after evaporation, and increasing the amount of acetic acid present to that prescribed in the regular method. In this work, 1·5 cc. of glacial acetic acid and 7·5 cc. each of cobalt acetate and sodium nitrite solutions were added, and the evaporations continued until the contents were pasty on cooling. The results obtained were :—

Chemically pure K_2SO_4—55·10 per cent and 54·84 per cent K_2O.
Chemically pure KCl—63·39 per cent and 63·52 per cent K_2O.

The plan of adding the acetate solution first seems to be the most promising one, and further work along this line may prove that this is a safe plan to follow, although as yet there has not been sufficient work done to draw definite conclusions. It is hardly necessary to add here that for the above work it is better to have chemically free potassium, or a blank is all the more essential for work of this kind.

The blank used in all the other work had remained constant, and never varied from 0·20 to 0·23 cc. N/10 $KMnO_4$ solution, but the blank here contained too much potassium from the chemicals used, it not being removed as it is in the ordinary nitrite reagent. As no purer chemicals were at hand, this work was discontinued, but it merits further investigation.

According to Bowser (*Journ. Am. Chem. Soc.*, xxxii., 78; CHEMICAL NEWS, ci., 100), the cobalti-nitrite method for qualitative tests for potassium is much more satisfactory when an equal volume of strong alcohol is added to the solution to be tested. In this manner, he claims that very small amounts of potassium are precipitated in much less time than from an aqueous solution.

From his work, the writer was led into a series of experiments to see if the above could be used for quantitative purposes. If such would prove to be the case, then the evaporation in the method would be eliminated, which would be a great improvement in the work.

Chemically Pure K_2SO_4.—The plan followed at first was to evaporate the solution containing 0·10 grm. of the salt to dryness. To the residue was added 5 cc. of the acetate solution, and then 5 cc. of the sodium nitrite solution already described. Ten cc. of alcohol were then added, and allowed to stand at ordinary temperature for the time indicated.

Time.	K_2O found (per cent).
15 minutes..	52·20
60 minutes..	51·99

The next plan tried was to evaporate the solution to about 5 cc. volume, and then add 10 cc. of the ordinary nitrite reagent and 15 cc. alcohol. In the first two determinations below, 0·1 cc. glacial acetic acid was added, and in the third no acetic acid. The solution stood at room temperature for the time indicated.

Time.	K_2O found (per cent).
Filtered immediately	50·78
5 minutes	50·80
15 minutes..	45·85

In the next experiments, the addition of the alcohol was omitted, and the work pursued along a different line. It had been found in working on the A. O. A. C. samples that the addition of more acetic acid than the directions called for had a tendency to give higher results in the regular method.

The plan was then followed of evaporating the solution containing 0·10 grm. aliquots to about 5 cc. volume, cooling, and adding 10 cc. of nitrite reagent, and the amounts of glacial acetic acid indicated. The solution was then allowed to stand for thirty minutes at room temperature.

A. O. A. C. Muriate.

Acetic acid added (cc.)	K_2O found (per cent).
1	48·98
5	50·38
15	Could not filter.

Evidently here, as in the regular method, an increase of acetic acid seems to give a higher result, but whether this increase is due to more potassium precipitated or to other causes is not easy to determine.

It was thought that perhaps the increase of acetates present in the solution influenced the precipitation of the potassium by the nitrite reagent, and to prove this, if possible, the following experiments were made on chemically pure KCl :—Two 0·10 grm. aliquots of the salt were taken, and to one, after evaporating to dryness, was added 10 cc. of a saturated solution of sodium acetate and 10 cc. nitrite reagent. To the other aliquot, after evaporating to about 5 cc. volume, was added 10 cc. reagent, and then 10 grms. of sodium acetate. Both were allowed to stand one hour at room temperature, and gave respectively 55·02 per cent K_2O and 48·34 per cent K_2O.

To determine if it was possible to completely precipitate the potassium at room temperature by this method, if the

volume of the solution was reduced, the following experiment was tried on chemically pure KCl :—

Two 0·1 grm. aliquots were evaporated to about 5 cc. volume, 1 cc. glacial acetic acid and 10 cc. nitrite reagent added, and the whole put in a desiccator over H_2SO_4, and the air exhausted as much as possible by means of the suction pump. It was then allowed to stand about twenty-four hours, and at the end of that time the solution had evaporated and the residue was nearly pasty. Result, 65·74 per cent and 67·52 per cent K_2O.

In every determination that has been made without heating the solution, it has been impossible to wash the potassium sodium cobalti-nitrite with water until the filtrate was colourless. While the washings did not contain any of the precipitate in suspension, they had a yellow colour which seemed to indicate that either the salt itself was dissolving, or, which is more probably the case, it was contaminated with some substance which made it difficult to wash clean. While it is easy to understand how low results are obtained while working in this procedure, the high results can only be explained on the supposition above, that the potassium salt contains some other compound that has been formed which is difficult to wash out, and reacts with permanganate.

From his experience with the Drushel modification of the cobalti-nitrite method, the writer believes that it is very accurate if properly handled, but an inexperienced worker not knowing its weak points may not have this opinion with his first use of it. Briefly stated, the outline of the method which has given the best and most uniform results in this work is as follows :—

The solution containing the potassium salt, after the preliminary work has been done to get it at this stage, is evaporated in a 500 cc. casserole to a small volume of about 5 cc., slightly acidified with acetic acid, and 15 cc. fresh nitrite reagent added. The larger amount of nitrite reagent makes possible a better filtration, and a good excess of reagent after the evaporation is made. The solution is evaporated on the water-bath for about forty-five to sixty minutes, or until the contents become a thick syrup while hot and pasty on cooling. Continued heating is to be avoided, and this is important to obtain good results. After the filtration is made and the casserole washed, the Gooch crucible and contents can be put in the same casserole and treated with permanganate, as prescribed in the method.

In conclusion, the writer desires to express his sincere thanks to Dr. A. M. Peter, of the Kentucky Agricultural Experiment Station, Lexington, Ky., for the valuable advice he has rendered during the progress of the work.

Non-inflammable Celluloid.—Dr. A. Eichengrün, of Berlin, has recently announced the results of his lengthy and exhaustive researches on acetyl cellulose. In 1901 he stated that the acetyl cellulose which was then the only acetyl derivative known, and which is soluble in chloroform, is not the tetracetate as was supposed, but the triacetate.. Further investigation, however, has shown that this view is hardly correct, and that a number of cellulose acetates exist which differ from one another in stability, solubility, &c. Some are soluble in chloroform, acetone, or acetylene tetrachloride, while others are completely insoluble. Cellite, which is an acetate soluble in acetone, is one of the technically most useful derivatives. From cellite thin films and leaves can readily be prepared, but acetyl cellulose has not the power of gelatinising. The author has, however, recently discovered a method of preparing acetyl cellulose solutions which, even when very dilute, gelatinise easily, and from which a plastic mass can be obtained which can be used for all the purposes of celluloid. The perfectly dry material externally resembles celluloid in all its characteristics, and can be obtained in all colours and qualities. This new substance, "cellon," is absolutely non inflammable, and simply melts when placed in contact with a naked flame.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Conversazione, *June 14th*, 1911.

The following were among the principal exhibits :—

Prof. Silvanus P. Thompson, F.R.S., and Prof. E. G. Coker. Experiments with Polarised Light.

1. A large polariscope. The field is 12 inches square, the polariser being a sheet of blackened glass.

2. Large scale experiments on optical stress in materials. The objects to be subjected to stress are cut out of xylonite, a substance which in polarised light shows the effects of stress by the production of interference colours of various orders.

3. Quarter-wave plates of mica. Cut from clear sheets of mica, supplied by Messrs. Wiggins. The largest is 19 inches in diameter. The two used in the experiments on stress, to produce an approximately circular polarisation of the light, are each 12 inches square.

4. Large scale polariscopic objects of mica, and selenite, and unannealed glass.

Prof. H. E. Armstrong, F.R.S., and Dr. E. F. Armstrong. The Action of Stimulants (Hormones) in promoting Enzymic Activity (Digestion).

The specimens shown are in illustration of results described in recent communications on "The Functions of Hormones in Stimulating Enzymic Change in relation to Narcosis and the Phenomena of Degenerative and Regenerative Change in Living Structures," and on "The Functions of Hormones in Regulating Metabolism." Like the barley grain, leaves are shown to be provided with protective differential septa through which strong acids, salts generally, and substances such as the sugars do not pass, but which are freely permeable by organic vapours, weak acids, ammonia, and a few salts (mercuric chloride, &c.). The passage of the excitant into the leaf is shown in the case of the common laurel (*Prunus laurocerasus*) by the liberation of hydrogen cyanide, and in the case of the spotted Japanese laurel (*Aucuba japonica*) by blackening due to the decomposition of the glucoside Aucubin. The active substances are for the most part non-electrolytes which have little, if any, chemical activity. The object of the exhibit is, in fact, to draw attention to the great physiological activity of substances commonly regarded as weak chemical agents.

Mr. Henry Crookes. Photographs and Living Cultures of *Bacillus Phosphorescens*, showing the germicidal action of some metals.

Nutrient gelatin-agar is poured into Petri dishes, containing small pieces of metal; when the medium has set, the surface is infected with *B. Phosphorescens*. After twenty-four hours the bacteria grow luxuriantly, except in a zone surrounding the piece of metal which remains entirely sterile. The extent of this death-zone varies with different metals.

The plates and photographs shown include silver, mercury, antimony, thallium, copper, gold, platinum, &c. Other bacteria are affected in the same manner.

Sir James Dewar, F.R.S. Radiometer Motion stopped by a very High Vacuum.

A Radiometer placed in a concentrated beam of the electric arc is stopped by a charcoal liquid air vacuum, and started again by mercury vapour given off by liquid mercury between the ordinary temperature and $-25°$ C., or at a limiting pressure of about one fifty-millionth of an atmosphere. Activity is again arrested on freezing out the mercury vapour by liquid air.

Mirrors formed by mercury distilling at the ordinary temperature. Illustration of the viscosity of the vapour of mercury at low presrures.

Dr. Deane Butcher. Examples of Osmotic Growths. Osmotic growths are mineral productions simulating the

forms of organic life. They are obtained by sowing a mineral seed or nucleus in a concentrated inorganic mother-liquor. The nucleus reacts with the liquid to form an insoluble gelatinous precipitate at the surface of contact. This semipermeable extensible membrane is distended by the osmotic pressure within, and grows by a process of intussusception, branching, and putting forth terminal organs as it reaches a solution of lesser concentration.

Osmotic growths were first described by Prof. S. Leduc in his work on the "Mechanism of Life."

Mr. A. Fowler, F.R.S. Spectrum Photographs showing the composition of the Tails of Comets.

The spectra of the tails of comets exhibit a number of double bands, which the photographs prove to be identical with bands obtained from vacuum tubes containing carbon monoxide at a pressure of about 0·01 mm. An additional band, due to nitrogen, was present in comet Morehouse.

Mr. A. Fowler, F.R.S., and Hon. R. J. Strutt, F.R.S. Spectrum of the Nitrogen Afterglow.

The photographs show the spectrum of the afterglow in comparison with that of the ordinary discharge through air or nitrogen. The spectrum of the exciting discharging is also shown.

Lowell Observatory, Arizona, U.S.A.

1. Photographic Negatives of Halley's Comet, taken at the Lowell Observatory, May 4th to June 5th, 1910.
2. Plates of Slit Spectrograms of Halley's Comet.
3. Plates of Slitless Spectrograms of Halley's Comet.

Three important deductions follow from the photographs and spectrograms:—

1. The identification, by Dr. Slipher, of the three chief bands in the comet's spectrum as those which Mr. Fowler, of the Royal College of Science, has shown to be the bands of carbon monoxide when under very low pressure.
2. The totally diverse gaseous constitution pointed out by Dr. Slipher between the emissive constituents of the head and tail—the bright gases of the one being strong where those of the other are weak and *vice versâ*.
3. Measurements by Professor Lowell on knots in the photograph showed an accelerated velocity away from the head, as follows:—

	Angular distance from the nucleus to the point measured in the tail.	Velocity of the point of the tail away from the nucleus.
Knot 1	1° 28′	13·6 miles a sec.
Knot 2	3° 12′	17·2 ,,
Knot 3	4° 36′	19·7 ,,
Knot 4	6° 15′	29·7 ,,

This, taken in connection with the spectrograms, disclosed the significant fact that the accelerated knots were composed, to the extent of 75 per cent of gases, not of solid particles, and that, therefore, *molecules* not only could be but actually were repelled by the action of the sun—contrary to current theory.

Sir William Crookes, O.M., F.R.S. Collection of Radiometers and Otheoscopes.

These experimental Instruments were made by the exhibitor during his researches on "Repulsion Resulting from Radiation," and were used to illustrate the papers when they were read before the Royal Society in the years 1875-78. Since 1878 they have been packed away in a cupboard, and only within the last few months have they been brought to light.

1. The first Radiometer, exhibited at the Soirée of the Royal Society, April 7th, 1875; with its original descriptive card. (*Phil. Trans. R. S.*, vol. clxvi., Pt. 2, p. 340; and Chemical News, April 30, 1875, vol. xxxi., p. 190).
2. Early Radiometer with glass arms and pith vanes. (*Phil. Trans. R. S.*, vol. clxvi., Pt. 2, p. 339).
3. Radiometer with upper tube to prevent the arms falling off the cup. (*Phil. Trans. R. S.*, vol. clxvi., Pt. 2, p. 354).
4. Radiometer with four aluminium vanes coated on one side with clear mica. No. 1338. January 1, 1878.
5. Radiometer with two aluminium vanes coated on one side with clear mica. No. 1338. January 1, 1878.
6. Radiometer with two vanes, each consisting of plates of polished iron and silver in close contact. No. 1279. October 12, 1877.
7. Radiometer having ten arms and carrying a light magnet. Used to communicate motion from the interior to the outside of the case and record the revolutions per minute, for photometric purposes. No. 818. (*Phil. Trans. R. S.*, vol. clxvi., Pt. 2, p. 354; *Proc. Roy. Institution*, February 11, 1876).
8. Large Radiometer with mica vanes, silvered on one side and lamp-blacked on the other. (*Phil. Trans. R. S.*, vol. clxvi., Pt. 2, p. 353).
9. Turbine Radiometer, having the vanes inclined at an angle. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, p. 112; Chemical News, April 7, 1876, vol. xxxii., p. 149).
10. Radiometer containing a double set of vanes, rotating in opposite directions. (*Roy. Soc. Proc.*, vol. xxv., p. 309).
11. Radiometer with aluminium vanes and movable screens of clear mica. Nos. 1043, 1288. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, pp. 89—93; and *Roy. Soc. Proc.*, vol. xxv., p. 309).
12. Radiometer with movable vanes driven by means of fixed screens sealed inside the glass bulb. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, pp. 119—120; and *Roy. Soc. Proc.*, vol. xxv., p. 310).
13. Spiral Radiometer. No 1245. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, pp. 114—115; and *Roy. Soc. Proc.*, vol. xxv., p. 310).
14. Radiometer with sloping vanes favourably presented to incident radiation, bulb filled with mercury vapour. (*Phil. Trans. R. S.*, vol. clxix., Pt. 1, p. 281; and *Roy. Soc. Proc.*, vol. xxv., p. 312).
15. Radiometer having cup-shaped vanes of aluminium, bright on both sides. No. 1293. (*Phil. Trans. R. S.*, vol. clxix., Pt. 1, p. 296; and *Roy. Soc. Proc.*, vol. xxv., p. 313).
16. Two-vaned radiometer in double bulb, with coloured liquid between. (*Phil. Trans. R. S.*, vol. clxvi., Pt. 2, p. 527).
17. Radiometer carrying a magnet and weighted with lead shot, for floating in water and showing rotation of the glass case when the vanes are fixed by a magnet. No. 1354. (*Roy. Soc. Proc.*, vol. xxiv., p. 409).
18. Radiometer the vanes of which are of pith coated on alternate sides with chromic oxide and precipitated selenium. Moves in one direction to heat rays and in the other to light. (*Phil. Trans. R. S.*, vol. clxvi., Pt. 2, pp. 266—272).
19. Spiral Radiometer. No. 1245. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, pp. 114—115; and *Roy. Soc. Proc.*, vol. xxvi., p. 310).
20. Radiometer with hemi-cylindrical aluminium vanes, bright on both sides. (*Phil. Trans. R. S.*, vol., clxix., Pt. 1, pp. 294—295).

The Otheoscope.

The Otheoscope (*ωθέω, I propel*):—"The glass envelope is an essential portion of the machinery of the radiometer, without which the fly would not move; but in the otheoscope the glass vessel simply acts as a preserver of the requisite amount of rarefaction. Carry a radiometer to a point in space where the atmospheric pressure is equal to, say, 1 mm. of mercury, and remove the glass bulb, the fly will not move, however strong the incident radiation; but place the otheoscope in the same conditions and it will move as well without the case as with it." (*Phil. Trans. R. S.*, vol., clxx., Pt. 1, p. 121).

21. Otheoscope with fixed vanes of oxidised copper, having a large horizontal disc of clear mica pivoted above it. The disc revolves under the influence of radiation from the copper when light shines on it. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, pp. 121, 122, 123; and *Roy. Soc. Proc.*, vol. xxvi., pp. 176—9).

22. Otheoscope, having a four-armed fly pivoted above a disc of bright aluminium. The vanes are driven round when light falls on the aluminium disc. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, p. 122).

23. Otheoscope, inclined vanes of clear mica driven by pressure from inclined vanes of blackened aluminium pivoted below. Under the influence of light the arms revolve in opposite directions. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, p. 123).

24. Otheoscope similar to No. 23, but having a pivoted disc above instead of clear mica vanes. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, p. 123).

25. Otheoscope, with four vanes of clear mica. Fixed to the side of the bulb are three plates of clear mica, equidistant from each other in a vertical plane, but oblique to the axis. Light falling on the fixed plates generates molecular pressure, which, falling obliquely on the fly, causes it to rotate. (*Phil. Trans. R. S.*, vol. clxx., Pt. 1, p. 120).

26. Instrument for showing the viscosity of the residual gas in a Radiometer. The lower disc of mica is connected with a magnet, and when this is put into rotation by means of an outside magnet the upper mica disc revolves in the same direction.

Prof. W. J. Pope, F.R.S. Photomicrography in Natural Colours.

Photomicrographs of rock sections, chemical preparations, and crystal interference figures are exhibited. The photographs were taken between crossed Nicol prism by the Dufay process, in which the colours of the objects are reproduced.

CHEMICAL SOCIETY.

Ordinary Meeting, June 1st, 1911.

Prof. Percy F. Frankland, LLD., F.R.S., President, in the Chair.

Messrs. Ralph Roscoe Enfield, Victor John Harding, and Arthur A. Eldridge were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Percy James Raymond, 20, Arboretum Road, Worcester; Ernest Vanstone, B.Sc., Gwynfe House, Mount Pleasant, Neath.

Of the following papers those marked * were read :—

*153. "*The Dissociation Pressures of the Alkali Bicarbonates.* Part I. *Sodium Hydrogen Carbonate.*" By Robert Martin Caven and Henry Julius Salomon Sand.

The dissociation pressures of sodium carbonate monohydrate and of sodium hydrogen carbonate have been examined by means of a specially designed tensimeter.

Difficulty was experienced in the latter case, particularly from the formation of impermeable crusts on the bicarbonate. Satisfactory results were obtained only when the amount of bicarbonate employed was four or five hundred times that theoretically required to evolve the necessary volume of gas at the highest temperature reached in the experiments.

It was found that the vapour pressure, in mm. of mercury, of sodium carbonate monohydrate can be represented with sufficient accuracy by the equation : $\log p = 10{\cdot}825 - \frac{3000}{T}$, and that of sodium hydrogen carbonate by the equation : $\log p = 11{\cdot}8185 - \frac{3340}{T}$.

From these equations the heat of dissociation of 1 grm.-molecule of sodium carbonate monohydrate is calculated to be 13,800 calories, and that of 2 grm.-molecules of sodium hydrogen carbonate to be 30,700 calories. The latter figure is in sufficient agreement with the number 29,700 calculated from thermochemical results given by de Forcrand (*Comptes Rendus*, 1909, cxlix., 719).

The pressures corresponding with the four phase equilibrium—anhydrous sodium carbonate, sodium carbonate monohydrate, sodium hydrogen carbonate, vapour—have also been calculated.

*154. "*The Absorption Spectra of Cinchonine, Quinine, and their Isomerides.*" By James Johnston Dobbie and Alexander Lauder.

The authors have examined the absorption spectra of cinchonine, quinine, and their isomerides, and find that each alkaloid gives two distinct spectra, A and B, the band in B being more sharply defined and much more persistent than the band in A. The spectrum A is obtained when the alkaloid is dissolved in alcohol or in water containing not more than one equivalent of acid to one of the base ; the spectrum B when it is dissolved in water containing at least two equivalents of acid to one of the base.

The difference between the two spectra was shown to be associated with the fact that the nitrogen of the quinoline nucleus is tervalent in the former, but quinquivalent in the latter case.

It was further shown that the spectrum A of cinchonine is practically identical with the spectrum of quinoline in alcohol, and the spectrum B with the spectrum of quinoline salts in aqueous solution. This is explained by the circumstance that the whole of the molecule of the alkaloid, except the quinoline nucleus, is, according to the generally accepted view of the constitution of the alkaloid, completely reduced, and reduced rings, as is well known, cause no selective absorption.

The absorption spectra of the isomerides examined are indistinguishable from those of cinchonine and quinine respectively.

*155. "*The Constituents of the Bulb of Buphane Disticha.*" By Frank Tutin.

Buphane disticha, Herb., is a bulbous plant, indigenous to South Africa, and has long been known to possess toxic properties.

The living inner portions of the bulb contain an abundant amount of alkaloid, whilst the dry outer layers are free from such a substance.

An alcoholic extract of the inner portions of the bulb, when distilled with steam, yielded a small amount of an essential oil containing furfuraldehyde.

The portion of the non-volatile product which was soluble in water yielded a small amount of acetovanillone (4-hydroxy-3-methoxyacetophenone), a quantity of chel donic acid, and considerable amounts of copper and lævulose. It also gave a mixture of alkaloids, the principal constituent of which is an amorphous strongly basic product, designated *buphanine*, which possesses a physiological action similar to that of hyoscine. A weakly-basic alkaloid, and one soluble in water, together with small amounts of narcissine, $C_{16}H_{17}O_4N$, were also obtained. The weakly-basic alkaloid is a convulsant poison, whilst the base soluble in water resembles colchicine and narcissine in its action.

Buphanine, on hydrolysis, is converted into a crystalline alkaloid, *buphanitine*, $C_{23}H_{24}O_6N_2$, which melts at 240°. *Buphanitine hydrochloride* and *methiodide* were also prepared.

The portion of the original extract which was insoluble in water consisted of amorphous products, together with pentatriacontane, a phytosterol, ipuranol, $C_{23}H_{35}O_2(OH)_2$, and a mixture of fatty acids, both free and combined.

*156. "*The Interaction of Formic Acid and Cellulose.*" By Charles Frederick Cross and Edward John Bevan.

Derivatives of cellulose obtained by direct interaction with formic acid, and also in presence of catalysts, have been investigated, and the quantitative data as to composition and decomposition (saponification both by alkalis and acids) are not reconcilable with the view that the products are simple esters of a normal cellulose.

Other modes of action of formic acid are known, and may explain the observed anomalies.

The interaction of cellulose and simple hydroxy-compounds was described, particularly in the case of resorcinol, which yields a well crystallised product, the alkaline solutions of which are crimson.

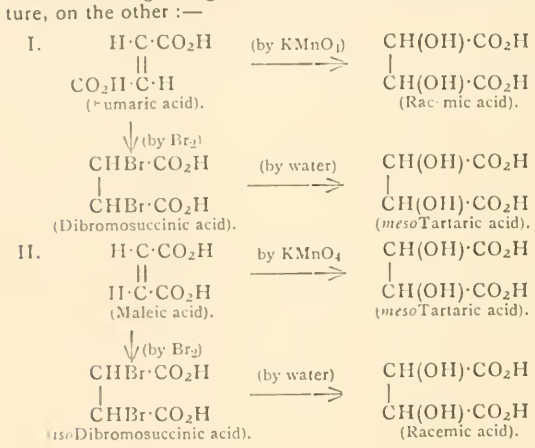
The quantitative data accord with a C_{13} formula.

This evidence, on the one hand, and the well known changes of the hexoses under the action of condensing acids on the other, were considered in relation to the interaction of formic acid and cellulose, in which more than one of the possible functions of the acid are involved.

*157. "*Configuration of the Stereoisomeric Dibromosuccinic Acids.*" (Preliminary Note). By ALEX. MCKENZIE.

Dibromosuccinic acid is formed by the action of bromine on fumaric acid, whilst maleic acid gives *iso*dibromosuccinic acid. Although a large amount of research has been devoted to these dibromo-acids, the question of their configuration had not been settled. Obviously, one of them must be resolvable into optically active components, and the other must be of the *meso*-type. The author finds that the *iso*-acid is the resolvable form.

The author was led to examine this problem by a consideration of the Walden inversion, on the one hand, and of the following changes, which are recorded in the literature, on the other :—



In the displacement of the halogen by the hydroxy-groups in these cases, it was conceivable that one had to deal with a change of configuration, or, in other words, with a process which was equivalent to a Walden inversion with optically inactive material. The other alternative was that the direct hydroxylation of fumaric and maleic acids with permanganate followed a stereochemical course of a different order from that followed by the direct addition of bromine. The experiments of the author are in favour of the latter view. Further, since the oxidation of fumaric and maleic acids by permanganate does not apparently lead to the formation of a mixture of *r*- and *meso*-tartaric acids, it appears likely that a change of configuration takes place during the addition of bromine.

*iso*Dibromosuccinic acid was prepared by the action of bromine on maleic acid in the presence of ether. The experimental conditions may be regulated so that practically no fumaric acid is produced, and the course of action depends to a remarkable degree on the quality of the ether used. The oxonium complex, $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!O\!<\!\begin{matrix}Br\\Br\end{matrix}$, described by Tschelinzeff, is possibly produced as an intermediate phase.

The ease with which the bromine in the *iso*-acid is displaced renders the resolution a difficult one. A partial resolution was, however, effected by means of morphine, using methyl alcohol as solvent.

Morphine (21 grms., 1 mol.) was dissolved in warm methyl alcohol (290 cc.), and, when the temperature of the solution was 46°, 19 grms. (1 mol.) of the *iso* acid were added in one instalment. The solution of the acid was immediately followed by the separation of glassy crystals of a morphine salt. After twenty-four hours at about 15°, the crystals (22 grms.) were removed. So far, it has not been found practical to crystallise further the salt which separates under these conditions. The resulting acid was strongly lævorotatory, giving $[\alpha]_D$ – 100·7° for c = 8·6 in ethyl acetate solution. The mother-liquor, from which the morphine salt had been removed, gave a dextrorotatory acid. 6·5 grms. of the acid with $[\alpha]_D$ – 100·7° were then treated with a solution of 7·1 grms. of morphine in 100 cc. of methyl alcohol. The resulting crystals (9·5 grms.) gave an acid with $[\alpha]_D$ – 114·5 for c = 7·4 in ethyl acetate solution. The latter acid (2·5 grms.) was again acted on by a solution of 2·8 grms. of morphine in 80 cc. of methyl alcohol. The yield of salt was 3·5 grms., and the acid from this gave the value $[\alpha]_D$ – 118° for c = 8·47 in ethyl acetate solution. So far, there is no evidence to show that this acid is the pure *l*-isomeride, and the work is being continued with the view of obtaining the latter.

DISCUSSION.

The PRESIDENT pointed out that the great interest attaching to Dr. McKenzie's investigation was that he had definitely fixed the Walden inversion as taking place in the passage from fumaric to dibromosuccinic acid and in that from maleic to *iso*dibromosuccinic acid respectively. In previously investigated Walden changes it was always uncertain whether the inversion took place in the introduction of the halogen or in its removal. Although in the present case the inversion took place in inactive material, it appeared to him that it was actually brought about by the presence of asymmetric groupings within the molecules concerned. Thus if, according to accepted views, the double linking in fumaric acid were opened up, for example, by the addition of two atoms of bromine, the normal result must be the formation of a *racemic* compound, and if instead a *meso* compound were produced it must depend on an atom of bromine and an atom of hydrogen exchanging places in one of the two halves of the molecule. Such an interchange could, according to accepted views on asymmetry, only be effected under the directing influence of asymmetric matter itself, as towards symmetric matter the two alternative groupings were in every respect equivalent. Such asymmetric directive influence appeared to him to be available in the present instance as soon as one atom of bromine had become attached, for the resulting asymmetric grouping $\begin{matrix}HO_2C\!-\!C\!-\!H\\\quad\quad\;\;|\\\quad\quad Br\end{matrix}$ would influence the configuration of the asymmetric grouping built up in the other half of the molecule, when the second atom of bromine became attached, with the result, as appeared from the author's experiments, that instead of the grouping $\begin{matrix}\quad Br\\H\!-\!C\!-\!CO_2H\end{matrix}$, there was obtained $\begin{matrix}\quad H\\Br\!-\!C\!-\!CO_2H\end{matrix}$.

The same reasoning applied to the formation of the racemic *iso*dibromosuccinic acid from maleic acid.

One was naturally led to inquire as to what asymmetric agency directed the transformation of one enantiomorph into the other In the case of the ordinary Walden inversions, and he wished to suggest that an asymmetric grouping which might exert such a directive influence was to be found in the probable combinations (by association or otherwise) of molecules of the optically active compound undergoing the halogenation of hydroxy- or amino-groups or the hydrolysis or amidation of halogen groups (these being the reactions in which the inversion had been found to take place). This hypothesis was in accord with the observations of Emil Fischer that optically active acids and their esters or their glycines often behaved differently, and again that different bases had different effects in respect of inversive action when used for the hydrolysis of optically active halogen compounds. Such different bases might be expected to alter profoundly the condition of

association or of other state of combination in which the halogen compounds might exist, besides altering the nature of the asymmetric grouping which was influencing the asymmetric group actually undergoing hydrolysis.

This hypothesis also indicated the possibility of a single enantiomorph (or the preponderance of one enantiomorph) emerging from a reaction in which an asymmetric grouping was, during a reaction, temporarily transformed into an unsaturated one.

Dr. Senter, with reference to the President's suggestion that the intermediate formation of bimolecular compounds might play a part in the Walden inversion, said that he had recently obtained evidence of the formation of such a compound, namely, $CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2Na$, in the hydrolytic decomposition of sodium bromoacetate. The final product, glycollic acid, was formed both by the hydrolysis of this compound and by the direct hydrolytic decomposition of sodium bromoacetate, in proportions depending on the dilution and temperature. As regards the further explanation of the formation of active compounds based on the assumption of the successive addition of bromine atoms at a double bond, it would be interesting to know if there was any direct evidence of such a mode of addition. The available evidence appeared to show that free oxygen, and also hydrogen, always combined as whole molecules, with subsequent rearrangement, but other elements, including the halogens, might behave differently in this respect.

158. "*The Influence of Conjugated Linkings on General Absorptive Power.* Part II. *Some Open-chain and Cyclic Compounds.*" By Cecil Reginald Crymble, Alfred Walter Stewart, Robert Wright, and Florence Williamson Rea.

In continuation of the previous work on this subject, an examination has been made of the absorption spectra of isomeric substances containing double bonds in different positions in the molecule. Eighteen spectra have been compared in the case of isomeric substances, and it has been found that in every case the conjugation of double linkings increases the general absorptive power of the compound. This influence is specially marked in the case of two other substances, namely, crotonic acid and allylacetic acid; for here, although the former compound contains fewer atoms and has the same number of double bonds, yet its absorptive power is very much more marked than that of the latter, in which the double bonds are not conjugated with each other. An attempt has been made to detect the influence on general absorption of two unsaturated groups placed far apart in a chain, but near together in space; the results, however, have not been positive.

159. "*New Derivatives of Aminolauronic Acid.*" By John Weir.

In the course of a research, the objects of which were: (1) the preparation of the camphor analogue of indigo—

$$C_8H_{14}{<}\begin{matrix}CO\cdot\\NH\end{matrix}{>}C{:}\,C{<}\begin{matrix}CO\cdot\\NH\end{matrix}{>}C_8H_{14},$$

and (2) the preparation of a diaminocamphor, $NH_2{\cdot}C_8H_{14}{\cdot}NH_2$, the following new compounds have been obtained.

1. *Carboxymethylaminolauronic acid*,

$$CO_2H{\cdot}C_8H_{14}{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

a crystalline solid, melting at 183—184°, and having $[\alpha]_D$ /18° in water +45·7°.

2. *N-Anhydrocarboxymethylaminolauronic acid*,

$$C_8H_{14}\begin{matrix}CO\\|\\N{\cdot}CH_2{\cdot}CO_2H,\end{matrix}$$

a crystalline solid, melting at 142—143°, and having $[\alpha]_D$/19° in water −22·2°, in alcohol −11·6°, and in benzene −22·2°.

3. *Anhydromethylaminolauronic acid*, $C_8H_{14}\begin{matrix}CO\\|\\NMe,\end{matrix}$ an orange-coloured wax.

4. *Benzoylaminolauronic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}NHBz$, a crystalline solid, melting at 204°, and having $[\alpha]_D$ 19° in alcohol −18·4°.

5. *Methyl benzoylaminolauronate*, a crystalline solid, melting at 88—89°, and having $[\alpha]_D$ /18° in alcohol −28·9°.

6. *N-Anhydrobenzoylaminolauronic acid*, $C_8H_{14}\begin{matrix}CO\\|\\NBz,\end{matrix}$ a crystalline solid, melting at 71—72°, and having $[\alpha]_D$ /18° in alcohol −69·1°.

The two main objects of the work were not realised.

160. "*The Triazo-group.* Part XVIII. *β Triazoethylamine.*" By Martin Onslow Forster and Sidney Herbert Newman.

β-Triazoethylamine, $N_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, obtained from the product of heating β-bromoethylamine hydrobromide with sodium azide, is a colourless oil, which distils at 63·5° (50 mm.), and has D_{16} 1·0488. It is reduced to ethylenediamine by stannous chloride in hydrochloric acid. The *hydrochloride*, with the *benzoyl*, *p-toluenesulphonyl*, *phthalyl*, and *p-nitrobenzylidene* derivatives, have been prepared, together with the *carbamide*, *phenylcarbamide*, and *phenylthiocarbamide*.

Unlike the corresponding halogen derivatives, β-triazoethylamine is not converted into dimethyleneimine by the action of the alkalis, thus offering an unusual contrast between the azoimide complex and the halogen atoms.

161. "*The Interaction of Metallic Oxides and Phosphoryl Chloride, alone and in the presence of certain Organic Compounds.*" By Henry Bassett, jun., and Hugh Stott Taylor.

Several metallic oxides react readily with phosphoryl chloride to give well defined double compounds. The following have been obtained: $CaO,2POCl_3$; $CaO,3POCl_3$; $MgO,2POCl_3$; $MgO,3POCl_3$; $MnO,3POCl_3$; $ZnO,3POCl_3$. These compounds crystallise well, but are very sensitive to moisture, for which reason they are difficult to obtain quite pure.

All the other oxides investigated (CoO, CdO, CuO, Cu_2O, HgO, Al_2O_3, Fe_2O_3) react more or less readily with phosphoryl chloride, but in these cases large quantities of the metallic chlorides are formed. The mechanism of this chloride formation was discussed, and reasons and experiments were brought forward which favour the view that it is preceded by the formation of an additive compound of the oxide and phosphoryl chloride.

The double compounds of metallic oxides and phosphoryl chloride yield a series of well crystallised derivatives with acetone, ether, and various esters, for example, $CaO,P_2O_3Cl_4,2Me_2CO$; $MgO,P_2O_3Cl_4,2CH_3{\cdot}CO_2Et$; $MnO,P_2O_3Cl_4,2CH_3{\cdot}CO_2Et$. These organic derivatives are quite easily obtained by dissolving the appropriate oxide in a solution of phosphoryl chloride in acetone, ethyl acetate, &c. Hydrogen chloride is liberated owing to the action of traces of moisture with formation of these derivatives of the compound $P_2O_3Cl_4$. Their ready formation supports the view that this compound is one of the first products of the action of moisture on phosphoryl chloride.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, June 12th, 1911.

Mr. E. Grant Hooper in the Chair.

The following papers were read and discussed:—

"*Observations on Cotton and Nitrated Cotton.*" (Part III.). By H. de Mosenthal.

The author shows by careful experiment that nitrocellulose does not dialyse, the previous experiments pointing in that direction having been misleading. Attempts to obtain a pressure indication with solutions of nitrated

cotton in acetone by means of the Pfeffer osmometer with different septa gave negative results.

Determinations of absorption spectra of a number of solutions of nitrocellulose and cellulose acetate kindly made by Dr. W. B. Tuck, in all cases showed a continuous spectrum shortened in the ultra-violet in proportion to the concentration, so that it can be stated that the cellulose group absorbs ultra-violet light.

In discussing the constitution of cellulose, the author shares the view expressed by Berl and Fodor that the dextro-cellulose of cotton is a polysaccharide, a condensation product of monose complexes. He suggests an open chain constitution formula based either on Green's formula or that of Vignon, giving preference to the latter. By opening Vignon's formula he shows that a concatenation of monoses could be conceived in which all the monoses were united by acetal linkages only, which would account for the facility with which cellulose is hydrolysed. It would, he thought, be more probable that acetal condensations occur in the plant than that ether linkages should be formed.

Both open formulæ correspond to the empirical formula, and by the addition of water innumerable celluloses or hydrocelluloses can be formed. The various pros and cons for this view are discussed.

"*Methods of Testing Inflammable Gas and Vapour Detectors.*" By A. PHILIP and T. STENHOUSE.

Miners, stokers, and others whose duties necessitate the use of safety lamps in certain danger areas are often extraordinarily ignorant of the kind of indication such lamps give when burning in air contaminated with inflammable gas or vapour. This state of affairs constitutes a real danger. The paper deals systematically with all the various methods of readily producing currents of mixture of air and inflammable gases and vapours.

These mixtures may be easily prepared of known and constant composition, and safety lamps may be burnt in test chambers through which currents of these mixed gases are caused to flow, and the conditions of the caps formed may be observed at leisure. These methods are particularly useful for class instruction, and also for determining and comparing the merits and demerits of all forms of inflammable gas and vapour detectors, whether of the flame cap variety or of that form in which the catalytic property of heated platinum is used, or indeed in any other form of detector. The cost of the apparatus for carrying out such demonstrations need not be greater than from £7 to £10, depending upon its make. It is not possible to give any adequate knowledge of the behaviour of the flame of a safety lamp when burnt in an atmosphere containing combustible gas or vapour by means of even the most detailed descriptions and drawings, whereas by the use of very simple apparatus the actual behaviour of such flames when burning in air contaminated either with the merest traces of combustible vapour or gas, or in any larger proportion up to mixtures which have explosive properties, may be rapidly and safely demonstrated. Students can easily adjust and work the apparatus themselves, and tests can be repeated again and again at trifling cost of either time or labour.

"*New Form of Automatic Inflammable Gas and Vapour Detector.*" By A. PHILIP and L. G. STEELE.

Inflammable gas and vapour detectors depending upon the catalytic action of platinum which have been used in the past have been found unsatisfactory for two reasons, firstly, the activity of the platinum changes in the course of time and use; that is to say, it becomes less sensitive in its action, or its behaviour becomes uncertain; whilst secondly, if the atmosphere into which this type of detector is introduced contains more than a certain proportion of combustible gas, the temperature of the catalytic platinum becomes so elevated that if it is a wire it fuses, and thus the mechanism of the device is completely broken down; or if the platinum is in the form of platinum-black, or spongy platinum, its surface becomes fused, and the sensitiveness of its action is thereby diminished.

The new instrument is so arranged that it automatically guards itself against any such dangers from overheating, whatever the proportion and nature of the mixture of combustible gas or vapour and air may be. The arrangement of the various parts of the detector cannot be made clear without diagrams, but the action of one of its forms depends upon the sensitiveness of a relay containing iron, and as the hysteresis lag in the iron tends to reduce the sensitiveness of the instrument, this lag is removed or reduced by either mechanically vibrating the relay or passing intermittent pulsating currents through it, which are superimposed on its normal currents.

This instrument is primarily designed to act as an automatic sentinel in danger areas, and as such will give a visual and audible alarm at any distance when as much as about one-fourth of the lower explosive proportion of combustible gas or vapour is reached. This detector has quite different functions from an ordinary safety lamp indicator, but gives equally sensitive indications which are more easily read than those of the best form of safety lamp flame cap indicators. The instrument can be installed at any desired distance from the point at which it is wished to test the conditions of the atmosphere.

ROYAL PHOTOGRAPHIC SOCIETY.

AT the meeting of the Royal Photographic Society on June 13th, Mr. E. SANGER SHEPHERD read a paper on the subject of the remedy for reversal, and brought forward the interim results of some photo-chemical investigations which have been carried out during the past five or six years by Mr. W. A. Caldwell, lately Professor at Cambridge.

These investigations, said Mr. Sanger-Shepherd, really amounted to the discovery of a new series of absorbers or sensitisers in photographic emulsion making, namely, the salts of hydrazine ($NH_2.NH_2$), made by adding a solution of acid to hydrazine hydrate. These salts were capable of absorbing the product of the reaction as quickly as the light affected the image, and their intervention made it necessary to reconsider the curve representing under, correct, and over exposure, which appeared with Hurter and Driffield's famous paper read before the Society of Chemical Industry twenty-one years ago. The particular salt of hydrazine differed for different emulsions. In the case of silver chloride many of the compounds were suitable, methyl-hydrazine, for example, while in that of silver bromide a more active compound was desirable, such as phosphorus acid salt of hydrazine.

On obtaining from Mr. Caldwell the first samples of plates to be made in this manner, Mr. Sanger-Shepherd said that he exposed a series of nine in the well known Hurter and Driffield rotating sector machine, starting with an exposure of 240 candle metre seconds and then giving an exposure four-fold, and still obtaining the correctly "stepped" negative. No matter how far he carried the exposure, he never got to that period which Hurter and Driffield called the period of decreasing rise or over exposure, and he never got reversal. He photographed an ordinary incandescent filament lamp, giving an exposure of ten minutes at F 22. The ordinary plate showed the image of the filament entirely reversed, while a plate from the same batch, but coated with hydrazine, gave the filament its correct gradation. In another case an arc lamp was given an exposure of 120 seconds, the actual arc on the non-hydrazine plate coming out dead-black, and on the other coming out white. A tangible result of all this would be to render it unnecessary to have two different classes of sensitive surfaces, as, for example, plates intended for development and papers intended for printing out. If it were true that the product of the reaction on exposing gelatino-bromide to light were effectually absorbed by hydrazine, it followed that it was possible to print out an image by the direct action of light upon the gelatino-bromide, and if the experiment were tried of taking a plate to which a compound of hydrazine had

been added, placing it in contact with the negative and exposing to the light, the result would be an image printed out by the direct action of light. After discussing other applications of hydrazine both to plates and papers, Mr. Sanger-Shepherd said that he had no doubt, provided sufficient exposure were given, they might always be sure of securing that perfect negative about which Hurter and Driffield were so anxious, and he did not think they need trouble either about over-exposure or reversal.

In reply to a number of questions, Mr. Sanger-Shepherd said that the addition of this substance to the emulsion had, if anything, a slight slowing action; that violent over-exposure would necessitate very weak development, but for twenty or thirty times' over-exposure ordinary methods of development would answer very well, and, finally, that the addition of hydrazine did not affect the spectrum negative and it could be used in conjunction with a dye for making a panchromatic plate.

NOTICES OF BOOKS.

A Course of Practical Work in Agricultural Chemistry for Senior Students. By T. B. Wood, M.A. Cambridge: University Press. 1911. (2s. 6d. net).

This pamphlet contains the full course of advanced work in agricultural chemistry which is done by the senior students of the University of Cambridge. It gives full and clear directions for the analysis of soils, fertilisers, dairy products, &c., by means of which students who had previously had a thorough training in general practical chemistry could successfully carry out all the ordinary qualitative examinations and quantitative determinations. The course covers a good deal of ground, and to work completely through it would represent many hours spent in the laboratory, and should result in a good practical knowledge of agricultural chemistry.

Cane-sugar. By Noel Deerr. Altrincham (Manchester): Norman Rodger. 1911. (20s. net).

The agriculture of the sugar-cane is treated very fully in his text-book, and the author's extensive experience of the practice of different districts enables him to discuss the cultivation of the cane from many points of view. One chapter is devoted to the consideration of the manuring of the cane, and another to the description of the pests and diseases to which it is liable. In this chapter, although limitations of space preclude the possibility of going deeply into the subject, some methods of fighting against the different diseases are mentioned, and a very complete list of references to periodical literature is appended. These references are a valuable feature of the book, and are added to every chapter. Methods of analysis are well treated, and a full bibliography is given with a list of experimental stations devoted to the investigation of questions connected with the sugar-cane industry.

Di Beziehungen zwischen Farbe und Konstitution bei Organischen Verbindungen. ("The Relation between Colour and Constitution in Organic Compounds"). By Dr. H. Ley. Leipzig: S. Hirzel. 1911. (8 marks).

The comprehensive researches on the relations between colour and constitution which have been published during the last few years are well summarised in this book, which while containing nothing very novel, nor contributing many important original results, gives a good outline of the work which has already been done on the subject. The author has done his best to avoid the insertion of all information of doubtful accuracy, to report only well established results, and to put the subject as far as possible upon a quantitative basis. He has devoted a comparatively large amount of space to absorption phenomena in the ultra-violet, after giving a detailed account of the chromophor theory, and discusses in an illuminating way the subject of colour changes in chemical transpositions and the colours of isomeric salts. In the second part of the book some methods of investigation are dealt with. Different types of spectroscopes are described with illustrations and hints upon their use, and some information is added on sources of light.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clii., No. 15, April 10, 1911.

Magnetic Properties of Fluorine.—P. Pascal.—From the study of benzene fluoride, C_6H_5F, and parafluophenetol, $C_6H_4F(OC_2H_5)$, it appears that fluorine is a diamagnetic element, the magnetic susceptibility of which is $3{\cdot}447 \times 10{-}7$, that of water being $-7{\cdot}5 \times 10{-}7$. The quantity $-3{\cdot}447 \times 10{-}7$ can be written $-10{-}7[14 \times 0{\cdot}2468 - 0{\cdot}008]$. The factor $-10{-}7 \times 0{\cdot}2468$ is also a factor of the magnetic susceptibility of many other elements, *e.g.*, carbon, sulphur, phosphorus, &c., and it seems probable that magnetic analysis will throw light upon the atomic structure of the diamagnetic elements.

No. 16, April 18, 1911.

Catalytic Etherification of Alcohols by Fatty Acids.—Paul Sabatier and A. Mailhe.—Titanic oxide is a more effective catalyser than thorium oxide in the direct etherification of alcohol by monobasic fatty acids, the action taking place at 150° in the case of formic acid. As the molecular weight of the acid is increased the degree of etherification is diminished. The yields obtained with secondary and tertiary alcohols are distinctly lower.

No. 17, April 24, 1911.

Hydrates of Potassium Fluoride.—M. de Forcrand.—Potassium fluoride dihydrate, $KF + 2H_2O$, is prepared by adding alcohol to a saturated aqueous solution of potassium fluoride and evaporating slowly. It melts at 41°, and it is difficult to obtain perfectly dry crystals, for it is fairly deliquescent, giving a liquid $HF + 4H_2O$ – $4{\cdot}5H_2O$ when left in the air. On rapidly evaporating a solution containing 4—4·5 H_2O below 20° large transparent crystals are formed containing exactly $4H_2O$. These crystals melt at 19·3°. The best way to prepare the hydrate with 4 molecules of water is to start with a solution containing $4H_2O$, and intoduce into it a little crystal of the tetrahydrate. The following are the heats of solution:—KF solid (anhydrous salt) 4·100 cal.; $KF + 2H_2O$ solid $-2{\cdot}140$ cal.; $KF + 4H_2O$ solid $-6{\cdot}160$ cal.

Synthesis of Secondary α-Ketonic Alcohols.—D. Gauthier.—In presence of 2 molecules of an organomagnesium compound R_2MgX Blaise's reaction yields with the oxynitriles $R_1—CHOH—CN$ a complex $R_1CHO(MgX) - C{\leqslant}^{NMgX}_{R_2}$, which is decomposed by water to give the compound $R_1—CHOH—CO—R_2$. The author has thus obtained good yields of several oxyketones, *e.g.*, 2-oxy-3-petanone, $CH_3—CHOH—CO—CH_2—CH_3$.

Synthesis of Oxyberberine.—Amé Pictet and Alphonse Gams.—When nitromethane acts on piperonal and the product is reduced, homopiperonylamine is obtained. With formaldehyde this gives norhydrohydrastinine, which condenses with methyl opianate. After saponifying the product and adding hydrochloric acid a crystalline precipitate is obtained, consisting of a mixture of orthonitrobenzoic acid and oxyberberine.

Condensation of β5-Dimethylglycidic Ether with Bromacetic Ether.—G. Darzens and J. Sejourné.—The condensation of dimethyl glycidic ether with bromacetic ether leads to the formation of α-oxy-α-isopropylsuccinic ether from which the acid can readily be obtained. The acid is remarkably stable, fairly soluble in water, very soluble in alcohol and ether, insoluble in benzene and petroleum ether. The authors have not yet succeeded in dehydrating it, even by treatment with phosphoric anhydride.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 4, 1911.

Action of Sulphur Dioxide on Ammonia.—Fritz Ephraim and Henryk Piotrowski.—When excess of sulphur dioxide acts on ammonia, amidosulphinic acid, $NH_2.SO_2H$, is formed; with excess of ammonia, according to the temperature, either white ammonium amidosulphite, $NH_2.SO_2.NH_4$, or a substance of the same composition but double the molecular weight results, $2SO_2.4NH_3$. This substance, which is red, is the triammonium salt of imidodisulphinic acid $(NH_4)N<^{SO_2NH_4}_{SO_2NH_4}$. Thionyl chloride and ammonia react according to the equation: $2SOCl_2 + 7NH_3 = 4NH_4Cl + NH<^{SO.NH_2}_{SO.NH_2}$.

Action of Sulphur and Compounds containing Sulphur on Hydrazine.—Fritz Ephraim and Henryk Piotrowski.—When sulphur dioxide acts on hydrazine the energetic reaction which occurs takes place according to the equation $2SO_2 + 3N_2H_4 = N_2H_2(SO_2N_2H_5)_2$, *i.e.*, the hydrazine salt of the hitherto unknown hydrazine disulphinic acid $SO_2H.NH.NH.SO_2H$ is formed. Hydrazine acts as a reducing agent on thionyl chloride and sulphur separates, subsequently dissolving in the excess of hydrazine to give "sulphohydrazinium." Sulphuryl chloride is hardly reduced at all by hydrazine. With sulphur trioxide hydrazine gives the sesquioxide S_2O_3. Hydrazine shows an enormous power of converting crystalloids into colloids.

Nitrosulphamide and Sulphohydrazide.—Fritz Ephraim and Eduard Lasocki.—Sulphamide can readily be nitrated by dissolving it in cold concentrated nitric acid. Hydrazine derivatives of nitrosulphamide can be obtained by the action of hydrazine hydrazincarbonic acid, $NH_2.NH.CO_2H.N_2H_4$, on sulphuryl chloride:—

$$SO_2Cl + 2NH_2.NH.CO_2H.N_2H_4 = \\ = SO_2(NH.NH_2)_2 + 2N_2H_4.HCl + 2CO_2.$$

Nitrosulphamide is a dibasic acid, and sulphohydrazide, $SO_2(NH.NH_2)_2$, also possesses two readily replaceable hydrogen atoms. Amidosulpho-acid, $NH_2.SO_3H$, cannot be nitrated, but its methyl ester can be obtained by treating it with ether and methyl iodide.

Lithium Imide.—Otto Ruff and Hans Goerges.—Lithium nitride and hydrogen react according to the equation $Li_3N + 2H_2 = LiNH_2 + 2LiH$. The mixture of lithium amide and hydride obtained when heated to 340—380° yields lithium imide and ammonia, and the latter immediately reacts with the hydride to give the imide and hydrogen.

Vanadium Chlorides.—Otto Ruff and Herbert Lickfett.—The following chlorides of vanadium are known, the last being the easiest to prepare:—VCl_2, VCl_3, VCl_4, V_2O_2Cl (?), VOCl, $VOCl_2$, $VOCl_3$. $VOCl_3$ is obtained by leading chlorine over a glowing mixture of the trioxide and carbon, or over the trioxide alone, or by leading chlorine and sulphur chloride or hydrochloric acid gas over the pentoxide. The tetrachloride is obtained when vanadium or vanadium carbide is heated in a current of chlorine. The trichloride VCl_3 is prepared by heating the oxychloride or tetrachloride or a mixture of both with sulphur, using a reflux condenser, and distilling off the excess of sulphur. When the trichloride is heated to a dark red heat in a current of nitrogen it yields the tetrachloride, which distils off, and the dichloride VCl_2 which remains behind. If the dichloride is heated in CO_2 to a dark red heat the same reaction occurs, $2VCl_3 \rightleftharpoons VCl_4 + VCl_2$, but on more strongly heating the oxychloride results, $3VCl_2 + 2CO_2 = 2VOCl + VCl_4 + 2CO$. At a still higher temperature the reaction is represented by the equation $4VCl_2 + 3CO_2 = V_2O_3 + 2VCl_4 + 3CO$.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 12th instant; The Duke of Northumberland, K.G., President, in the Chair. Miss A. Carthew and Lieut.-Colonel A. W. H. Hornsby-Drake were elected Members. The Special Thanks of the Members were returned to Mr. W. Phipson Beale, K.C., M.P., for his donation of £25 to the Fund for the Promotion of Experimental Research at Low Temperatures; and to Dr. Donald W. C. Hood, C.V.O., for his present of a portrait of Faraday. The Chairman reported the decease of the Dowager Duchess of Northumberland, and a resolution of condolence with the family was passed.

Who's Who in Science.—The need of a book of reference containing the names, appointments, and achievements of the world's foremost scientists has long been felt in learned circles. Messrs. J. and A. Churchill have in preparation a new annual which is designed to meet this want. It will be called "Who's Who in Science," and is to be edited by Mr. H. H. Stephenson. Schedules are now being addressed to the scientists whose names may appear, and it is hoped that they will assist the publication by filling in and returning the forms to 7, Great Marlborough Street, London, W., as soon as possible. For enabling scientists to communicate with each other all the world over, and for giving a rapid summary of the achievements and careers of great men, the new annual should soon prove itself indispensable. Writing to the publishers, Sir E. Ray Lankester, K.C.B., F.R.S., says:—"I feel sure that your new publication will be a great convenience to all who are engaged in scientific work and in literature connected with it. I wish you every success in this new enterprise."

MEETINGS FOR THE WEEK.

WEDNESDAY, 28th.—Microscopical, 8. "Structure of Scales from *Thermobia domestica*" and "Description of a Model producing an Optical Effect similar to the Cuneate Markings in Insect Scales," by J. Strachan. "Rotifera of New Zealand and South Africa," by J. Murray. Exhibits—Interferometer, by C. Beck; Prof. E. Emrys-Roberts' New Microscopical Lamp, by The General Electric Company; Slides of Diatoms, by the Society.

THURSDAY, 29th.—Royal Society. "New Method of Estimating the Aperture of Stomata." by F. Darwin and Miss D. F. M. Pertz. "Memoir on the Theory of the Partitions of Numbers—Part VI., Partitions in Two-dimensional Space, to which is added an Adumbration of the Theory of the Partitions in Three-dimensional Space," by Major P. A. MacMahon. "The Kinetic Theory of a Gas constituted of Spherically Symmetrical Molecules," by S. Chapman. "Radiation in Explosions of Coal-gas and Air," by W. T. David. "Mechanical Viscosity of Fluids," by T. E. Stanton. "A Silica Standard of Length," by G. W. C. Kaye. "Properties of Oil Emulsions," by R. Ellis. "A Class of Parametric Integrals and their application in the Theory of Fourier Series" and "A Mode of Generating Fourier Series," by W. H. Young. "Pendulum Clocks and their Errors," by A. Mallock. "On Ceratopora, the Type of a New Family of Alcyonaria," by S. J. Hickson. "Sensibility of the Eye to Variations of Wave-length," by W. Watson.

FRIDAY, 30th. Physical Society, 5. "Effect of a Narrow Saw-cut in the Edge of a Conducting Strip on the Stream Lines in the Strip and on the Resistance of the Strip," by C. H. Lees. "Capacity Coefficients of Spherical Electrodes," by A. Russell. Exhibition of the Benkö Primary Battery, by W. R. Cooper.

THE CHEMICAL NEWS.

Vol. CIII., No. 2692.

THE CAUSES OF ABSORPTION OF OXYGEN BY THE LUNGS IN MAN.*

(Preliminary Communication).

By C. GORDON DOUGLAS, B.M., Fellow of St. John's College, and J. S. HALDANE, M.D., LL.D., F.R.S., Fellow of New College, Oxford.

In a previous communication (*Roy. Soc. Proc.*, 1910, B, lxxxii., 331) we gave a short account of experiments on mice, showing, by the carbon monoxide method of determining the partial pressure of oxygen in the arterial blood, that when want of oxygen is produced by administering to these animals a relatively high percentage of carbon monoxide in the air breathed, active secretion of oxygen inwards through the lung epithelium occurs, although in resting animals the passage inwards of oxygen is apparently due to nothing but simple diffusion.

It was very desirable to extend these experiments to man, as the main chemical factors in respiration can be much more satisfactorily investigated in man than in lower animals, and we have now succeeded in obtaining a number of results in man. In the case of a man it would require many hours to complete an experiment made by exactly the same method as was employed for mice and rabbits. We have therefore adopted the plan of first rapidly administering sufficient carbon monoxide to bring the blood to the required degree of saturation with the gas, and then allowing the subject to breathe into a closed space of about 15 litres, in the air of which the carbon dioxide is absorbed and the oxygen kept constant on the principle of Regnault and Reiset. The partial pressure of carbon monoxide in this air becomes equal in a few minutes to that in the blood, and part of this air is thereafter used for saturating the sample of the subject's blood, the principle of the experiment being otherwise the same as in the experiments on animals. The following results have been obtained: —

1. During rest under normal conditions, and provided that the blood is not more than about 25 per cent saturated with carbon monoxide, the partial pressure of oxygen in the arterial blood is practically identical with that in the alveolar air. This result accords completely with the theory that under these conditions the absorption of oxygen is by diffusion alone.

2. When the percentage of oxygen in the inspired air is lowered sufficiently (or the saturation of the blood with carbon monoxide is increased sufficiently) to cause appreciable symptoms of want of oxygen, the partial pressure of oxygen in the arterial blood becomes very considerably higher than in the alveolar air. Active secretion of oxygen inwards is therefore occurring, as was formerly concluded by Haldane and Lorrain Smith from experiments on mice. We find, however, that Haldane and Lorrain Smith's results require a considerable and at present somewhat uncertain correction.

3. During muscular work also, unless the work was of a comparatively gentle kind, a similar result was obtained, and muscular work with the inspired air poor in oxygen seemed to produce a specially striking effect.

Taken together, the results indicate that the lung epithelium is excited directly or indirectly to active secretion of oxygen inwards by products of metabolism proceeding from the muscles and other tissues when their oxygen supply is insufficient to meet ordinary requirements. That such insufficiency actually occurs during muscular work, and when air with a low partial pressure of oxygen is breathed, has already been shown (Geppert and Zuntz, *Pflüger's Achiv.*, 1888, xlii., 189; Boycott and Haldane, *Journ. Physiol.*, 1908, xxxvii., 355; Ogier Ward, *Ibid.*, xxxvii., 378; Haldane and Poulton, *Ibid.*, xxxvii., 390; Douglas and Haldane, *Ibid.*, 1909, xxxviii., 420; Ryffel, *Ibid.*, xxxviii., 29; Boycott and Chisolm *Biochemical Journ.*, 1910). These results are of special interest in connection with the phenomena of adaptation to very high altitudes, and throw a new light on the physiology of mountain climbing and balloon ascents, and of ordinary muscular work.

* A Paper read before the Royal Society, March 23, 1911.

POWER AND ITS APPLICATIONS.

At the Extraordinary Meeting of the New York Section of the American Electrochemical Society held on Saturday, March 18, the Chairman, Mr. Elmer A. Sperry, made the following remarks:—

In the realm of power and its myriad applications we have what probably constitutes the greatest single advance of modern times. In this age of electricity it has often fallen to my lot to be more or less intimately acquainted with the phenomenal and wonderful advances in this field—advances taken by leaps and bounds; in single decades advances have been made equal to whole centuries in many other lines of activity.

In the spring of 1884 I became the only Western delegate to come to this city from Chicago, to help in organising the American Institute of Electrical Engineers. A small group of us gathered in the modest rented quarters of the then young Society of Mechanical Engineers, and I became the fifth to sign the charter. A small group of earnest men worked wiser than they knew in thus organising a society which has since become a body of international importance, its members now numbering upwards of 7000.

It must be remembered that at this time the only practical and commercial application of electricity was in lighting. In the spring of the next year it so happened that I was chairman of the Committee of Call of the first convention of the National Electric Light Association, which we organised in the city of Chicago in 1885, and which is now a flourishing organisation, having some 8000 members doing a vast work in many fields of practical application of electricity, especially leading in the work of conservation of all natural sources of power throughout this country.

The art and industry which we foster represents the most direct and most recent development of this great advance movement in the direct application of power, in that we bring power or energy in its most controllable, as well as its most active form, namely, electricity, to bear upon chemical actions and reactions, resulting in many fields in a much more direct and economical solution of the problems involved; in numerous instances, in products otherwise unattainable and working economics which at once place valuable elements and compounds within reach of all, thus rendering great service to mankind.

Electrochemistry, as such, may be said to be American in its origin, and emphatically American in its development. I speak advisedly on this point. Our great water power resource and development is not alone responsible for this; the enterprise and enthusiasm of our technical and commercial men has played no small part in this great work. Such names as Castner, Hall, Wilson, Acheson, Herreshoff, Townsend, Dowe, Gibbs, and a host of others testify to this. As to this art being American in its development one has only to recount the numerous chemical processes we have imported bodily from Europe, and almost without change adopted. Outside of this long list it should be remembered that we are still currently importing a large amount of chemical products. The contrast with this quite strikingly emphasises the point that we make—that

in the field of electrochemistry we have been enabled to very largely supply the entire demand for electrochemical products and cut down very materially, if not cut out entirely, the importations.

The value of the electrochemical, as compared with the purely chemical method, is illustrated by the "Solvay" process, which was imported from Belgium, and which employs as its principal raw material sodium chloride or common salt; but in the operation of this process only one of the elements of this valuable compound, namely, the sodium, is recovered. Our State was recently called upon to condemn and to relinquish a lake of quite considerable size for receiving the deposit containing the other element, namely, chlorine, which is a waste product rejected in this process. In a number of electrolytic plants in this country where the same raw material is employed practically 100 per cent of both of these constituent elements are recovered and rendered available and useful, certainly marking an advanced movement in the point of conservation of our mineral resources. This illustrates one only of the advantages following the direct application of electricity in processes that are known as "electrolytic." Our good Mr. Herreshoff here present tells me that practically 90 per cent of all the copper that is used in the world is refined electrolytically. Seventy or 80 per cent of the original copper contains arsenic, minute quantities of which are known to degrade copper and render it practically useless as an electrical conductor. The electric arts employ about 70 per cent of all the copper produced; thus the circuit may be said to be closed in two ways—electrolytic ministering to the electrical.

There is quite a dramatic aspect connected with this electrolytic copper refining not popularly understood. Think of 900,000 tons of this beautiful glistening red massive metal existing as a perfectly clear watery solution in one stage of its life history, during its transit from anode to cathode after it has been dissolved by the direct action of electrical energy in the electrolyte.

Started in Germany, this process was taken up actively in England, but now it may be said that America is its only home; certainly by far its greatest activity is to be found here, and we have here present probably the greatest worker in this art—certainly the one who has brought to its highest perfection the electrolytic copper refining.

Again, electrolysis has given the world aluminium. Only a few years ago this metal was 6.00 dols. a pound. Then it gradually came down to 1.00 dol. The engineering world then gave its use the first passing thought. Hall, working on and on, through many discouragements, succeeded finally by its electrolytic production, by the direct application that this method affords, in supplying the energy for which this element has an enormous appetite, and so reducing its cost as to place it within reach of all. In consequence its industrial applications have broadened, until 50,000 tons, valued at 20,000,000 dols., are annually consumed. This metal also, like the copper, is in the form of a perfectly clear solution in one stage of its life history, with this difference, however, that in the case of the copper, the solution stage constitutes what may be termed its "graduation certificate," whereas with aluminium it is even more far-reaching and actually constitutes its "birth certificate."

I might go on enumerating interesting examples of these direct applications of electricity for producing chemical reaction, both in electro-chemical and thermal applications, which constitute the principal activities and interests of our members. For instance, a most valuable product, calcium carbide, would not exist were it not for the electric furnace, this process having been discovered and brought out in this country by Mr. Wilson.

One fact which arrested my attention, however, and for which I crave your indulgence for a moment more, is a fact brought out recently by a noted authority in the field of organised research, the next speaker, Dr. Whitney, of Schenectady, when he stated that it was a fortunate circumstance when bodies were organised or otherwise induced to react, they did not directly tend, in the majority of cases, to reproduce the energy, or energy of the same form; for instance, reactions do not tend directly to produce heat, but, on the contrary, when energy, such, for instance, as heat or electricity, is applied, and a reaction takes place, a new compound is produced; that is, the operation "side-steps," so to speak, bringing about a new and, broadly speaking, an unexpected result. This phenomena of indirection, as it may be called, seems to me to be a general law, a sort of a by-pass which nature takes in producing variety.

It may be stated that this is the manner in which variety occurs. So universal is this method that, as a matter of fact, it is difficult to obtain a reaction which does give back the energy in the same form as applied.

The universal law seems to be one of translation instead of oscillation. In fact, upon introduction, stresses will give you almost anything except a return of the particular stress qualitatively. This phenomena having such a very striking and complete homologue in a totally different branch of science and one to which I have devoted considerable attention, I may be pardoned if I bring it to your attention by the use of a model which serves to illustrate in a most vivid way just what I mean. I hold before you a gyroscope having Cardian or universal mountings; the outer ring being pivoted, I now swing it back and forth, and we see the inner ring which is mounted therein, and its wheel simply partakes of the same motion, and that nothing whatever peculiar occurs; that is, all of the parts move together, just as they should, back and forth, upon the pivots of the outer ring. But suppose I now spin up the wheel within its inner ring, and repeat the same operation; that is, attempt to swing the outer ring to and fro upon its pivots as before. Our attention is at once arrested by the very peculiar vigorous and unexpected motion which the inner ring now makes. It is evident that this motion is not only automatic, being self developed, but it seems to bear no relation whatever in this direction to that of the impressed forces, and upon closer examination we find that it exists to the normal, or actually at right angles to the line of the original energisation. As a matter of fact, it "side-steps," and this it does invariably. With each application of stress in a given line or plane, the inner ring moves to and fro in a plane at right angles, "side-stepping," so to speak, under the impressed stress, and in a line or direction just as far removed from that of the impressed forces as it is possible for it to do, namely, 90°, measured either uniplanar or as a spherical function. Here we have this phenomenon in a form which we can handle, study, weigh, and measure. The homologue, I believe, has a very far-reaching significance, and one which I cannot but believe derives its fundamental activity in this devious path from the same underlying principle, namely, rotation. It need not be rotation about its own axis, as in the case of the inner wheel before us, but it may be rotation about a remote centre of which the observer has no knowledge, nor the existence of which he even suspects; yet all that is required is the presence of rotation or angular velocity, and when this is present in either ion, atom, molecule, or mass, there invariably exists a definite and powerful tendency; a definite ponderable moment of effort in this new direction to one side practically at right angles to that of the stress or forces impressed. These phenomena are not only quantitatively analogous, but I believe them to be quantitative and determinable.

Nor should we look upon such a solution of this action, which seems almost universal, as less significant. When we remember that motion itself is universal, all nature seems to be either in state of motion or consisting of motion in its deeper significance.

As the underlying principles of these motions are better understood, why should we not be able to assign definite values, to pre-cast definite directions in which the movements or reactions should proceed, and with the same degree of precision that we are now enabled to apply in that branch of the useful arts in which this self same

phenomenon is fundamental is just now in rapid state of development, and is destined to become an extremely important and useful force in the service of mankind.

I hope that this seeming digression may be pardoned. By the use of the model I have endeavoured to make clear to you the true nature of this phenomenon, the strange physical reaction which we know as gyroscopic precession. Knowledge of this action was made use of by our great contemporary J. J. Thomson in a number of notable observations made not long since, and I am hoping that it may so impress itself upon your minds as to be equally useful to you. It should not be understood that the observations and statements I have made are put forward as being in any way final, but are intended to be more in the line of suggestion.

ON THE SEPARATION OF CERIUM BY POTASSIUM PERMANGANATE.

By EDWIN J. ROBERTS.

One of the most useful methods for the separation of cerium from the rare earth metals which accompany it depends upon its oxidation by potassium permanganate, according to the equation—

$$3Ce_2O_3 + 2KMnO_4 + H_2O = 6CeO_2 + 2KOH + 2MnO_2.$$

This action takes place in a cerous nitrate solution provided some neutralising agent is present to take up the nitric acid set free. Stolba, in 1878, used zinc oxide for this purpose (*Jahresber.*, 1878, p. 1059), and other investigators have since used the method (Muthmann and Rölig, *Ber.*, xxxi., 1718; James, *Journ. Am. Chem. Soc.*, xxx., 982). Drossbach (*Ber.*, xxix., 2452), Böhm (*Zeit. Angew. Chem.*, 1903, p. 1129) Muthmann and Weiss (*Ann. Chem.*, cccxxxi., 9), Meyer (*Zeit. Anorg. Chem.*, xxxvii., 378), and others have used alkali hydroxides or carbonate in place of zinc oxide. More recently, Meyer and Schweitzer have studied this process, using sodium carbonate (*Zeit. Anorg. Chem.*, liv., pp. 104—120). They give the equation—

$$3Ce(NO_3)_3 + KMnO_4 + 4Na_2CO_3 + 8H_2O = 3Ce(OH)_4 + Mn(OH)_4 + 8NaNO_3 + KNO_3 + 4CO_2,$$

and use two different solutions for the precipitation. One, for the complete removal of the cerium, contains one molecule of permanganate to nearly five of sodium carbonate; the other, for the purification of the cerium, contains one molecule of permanganate to less than three of sodium carbonate. It is obvious from the above equation that in the first case large amounts of other earths will be precipitated with the cerium by the excess of alkali, while in the second case the nitric acid will be in excess at the end of the process, leaving considerable amounts of cerium in solution. The object of the present work was to study the process carefully and to produce, if possible, a sharper separation of the cerium.

When a little potassium permanganate solution is added to a hot neutral solution containing cerous nitrate, the red colour of the permanganate is instantly bleached, and a brown precipitate appears. If the addition of the permanganate is continued, the colour is bleached more and more slowly, the liquid becomes distinctly acid to litmus, and finally the red colour becomes permanent. If a little alkali is now added, the colour is again bleached, and if the liquid is kept neutral, or very nearly so, the red colour will not be permanent until all the cerium is precipitated. The action seems to be as follows:—The cerous nitrate is oxidised by the permanganate, probably according to the equation—

$$3Ce(NO_3)_3 + KMnO_4 + 3H_2O = 2Ce(NO_3)_4 + Ce(OH)_4 + KNO_3 + H_2MnO_3 \quad . \quad . \quad 1.$$

The ceric nitrate formed then hydrolyses—

$$Ce(NO_3)_4 + 4H_2O \rightleftarrows Ce(OH_4) + 4HNO_3 \quad . \quad . \quad 2.$$

If no alkali is added, the accumulation of nitric acid in the liquid checks the process by reversing the action in Equation 2, and also in Equation 1, for when a little of the mixed precipitate of hydrated ceric and manganese dioxides was treated, after washing, with dilute nitric acid and warmed, a strong permanganate colour was produced. The addition of alkali at this point of course simply removes the free acid, and allows the action to become complete. The fact that the oxidation and precipitation take place even in the presence of appreciable amounts of free nitric acid makes it possible to secure a better separation than would otherwise be the case; for if the liquid is kept perfectly neutral the small amounts of trivalent earths which are locally thrown down by the alkaline precipitating solution will not be re-dissolved, while if the liquid is distinctly acid during the whole process they will tend to re-dissolve on stirring. These considerations give the theoretical conditions for the process. As to the choice of a neutralising agent, it is of course desirable to use no compound of a metal which is precipitated by oxalic acid, or which is not easily separated from the rare earths, as, for example, zinc oxide or calcium carbonate. Magnesium oxide was tried, but does not give as good results as the alkali carbonate, and is not so easily controlled. Sodium carbonate seems to be the simplest and most convenient neutralising agent for the purpose.

The solution used for the precipitation is made by dissolving 158·03 grms. (1 mol.) of potassium permanganate and 424·00 grms. (4 mols.) of dry sodium carbonate in any convenient amount of water. The solution should be kept in glass-stoppered bottles, and should not be allowed to come in contact with organic matter. Solutions of pure permanganate and of pure sodium carbonate, of any convenient strength, are also needed. The process is carried out as follows:—The rare earth solution, which should not contain other salts than nitrates, is heated to boiling in a large porcelain dish, and, if not already neutral, is neutralised with the sodium carbonate solution. The solution of permanganate is added in small quantities until the red colour just begins to be permanent, and the mixed solution of permanganate and alkali is then added very slowly, with constant stirring, the liquid being kept nearly at the boiling-point during the whole process. A faint colour of permanganate is maintained all the time in the liquid, a little of the pure permanganate solution being added if at any time the colour is entirely bleached. This is important, as the constant acidity of the liquid is thereby insured. When the cerium is nearly all precipitated, the colour is bleached more slowly after each addition of the precipitant, and the effervescence is less noticeable. The acidity of the liquid should now be tested from time to time, which may be done with litmus-paper if only a slight excess of permanganate is present. Small amounts of the mixed solution or of sodium carbonate are added, until the liquid is nearly neutral to litmus, and still is faintly coloured with permanganate. The whole is heated, and stirred for about ten minutes, and filtered hot. The precipitate is washed with boiling water till the washings give no precipitate with ammonia. If the liquid at the end of the precipitation is faintly acid, the filtrate usually contains a trace of cerium giving a faint yellow colour with ammonia and hydrogen peroxide, while from the precipitate a preparation of cerium chloride may readily be obtained which shows no absorption bands in a thickness of 15 cm. of very concentrated solution. The presence of a little cerium in the filtrate, where the earths in the latter are to be subjected to fractional crystallisation, is usually not objectionable.

To ensure the complete removal of the cerium, the liquid at the end of the precipitation must be made absolutely neutral, when a filtrate is obtained which gives no test for cerium with hydrogen peroxide. Before testing, the excess of permanganate is removed from the filtrate by boiling with a few drops of alcohol. After re-filtering, the other earths are precipitated by oxalic acid. The precipitate of cerium and manganese hydroxides is dissolved in strong

hydrochloric acid, the solution diluted and precipitated with oxalic acid, and the cerium oxalate re-converted to nitrate. On repeating the process with this material, a pure cerium preparation is obtained, which gives an oxide of the characteristic pale yellow colour. The process was thoroughly tested on several different kinds of material. A mixture containing as much as 35 to 40 per cent of praseodymium and neodymium yielded pure cerium in two operations.

Attempts were also made to extract the first cerium and manganese precipitate with dilute nitric acid, in order to remove the last traces of praseodymium and neodymium without recourse to a second permanganate treatment. The precipitate obtained in the usual manner was thoroughly washed on the filter, then transferred to a large dish, and heated nearly to boiling with a large volume of water. Nitric acid was then added carefully until the liquid began to show the permanganate colour. The whole was heated for about fifteen minutes, and the precipitate filtered off and washed. This cerium preparation, when freed from manganese, gave a pale reddish oxide, showing that the neodymium and praseodymium are not entirely removed from the first precipitate by extraction with dilute nitric acid.—*American Journal of Science*, xxxi., May, 1911.

THE BACILLUS OF LONG LIFE.

By LOUDON M. DOUGLAS, F.R.S.E., Edinburgh.

MANY people are under the impression that the use of soured milk is of recent origin, and at the present time this practice is often referred to as one of the latest fads.

This is, however, far from being true, as we have abundant evidence to show that in many tropical and semi-tropical countries the daily use of soured milk in some form or other (Kephir, Koumiss, Yoghourt, Leben, &c.) has been practised for many centuries. The natives of Bulgaria, Servia, Turkey, Egypt, Mongolia, and India have been accustomed from time immemorial to systematically sour their milk, and the researches of recent years have shown this custom to be practically and scientifically justified, and to be the prime factor in the attainment of the longevity enjoyed by such people.

I have only recently had an opportunity of witnessing in Turkey, Bulgaria, Servia, and throughout the Balkan States of Europe how much soured milk enters into the daily diet of the people, and can very well understand now how its potent influence has come to be recognised.

Why the Use of Soured Milk is Beneficial.

It is a matter of common knowledge that bacteria, microbes, or germs may be divided into four classes, viz. :—

(*a*) Useful bacteria, as used for souring cream, ripening cheese, making vinegar, &c.
(*b*) Putrefactive bacteria, which rot or decompose foods, and often cause ptomaine poisoning.
(*c*) Disease producing bacteria.
(*d*) Indifferent bacteria.

With the two latter groups we have nothing to do at present, but it may be said that it is rapidly becoming more and more apparent that, if we would maintain a good state of health, the growth of putrefactive organisms in food must be reduced to a minimum.

The preservative action of lactic acid upon meat, milk, butter, and cheese has long been known, but we are indebted to Prof. Metchnikoff for the introduction of a method of checking the growth of putrefactive organisms in the human body, by the administration of lactic acid-producing bacteria.

Although numerous species of lactic bacteria are met with in ordinary milk, and cause the normal souring or curdling of milk in warm weather, yet these are not suitable for artificially souring milk for therapeutic purposes.

In the first place, they are not capable of producing sufficient acid ; and secondly, they are incapable of growth at the temperature of the body, and hence do not exert any influence upon the putrefactive organisms in the digestive track.

It was necessary, therefore, to search for a strong acid-producing organism, and one requiring a high temperature for growth. Such an organism was found in Bulgarian soured milk, and has been named the *Bacillus Bulgaricus* or the "Bacillus of Massol" ; more recently it has been termed the "Bacillus of Long Life." By the growth of this organism in the intestinal track, most of the injurious putrefactive bacteria are destroyed, and the production of poisonous by-products causing auto-intoxication comes to an end.

There have been many preparations of *The Bacillus* offered to consumers, and lactic acid organisms have been administered in chocolates, tabloids, powders, in dates, and in other ways, but the most natural method is that of the administration of an actively growing culture in milk, and it has given the most satisfactory results. It is essential that the culture should be pure.

The Preparation of Soured Milk.

In order to prepare reliable soured milk it is necessary to observe various precautions, or failure will ensue. Milk produced under ordinary conditions contains enormous numbers of bacteria, which have been derived from the air, dust, hairs, &c. These bacteria multiply with great rapidity, and, under suitable conditions, the milk becomes curdled within a few hours, assumes an acid or bitter taste, and is often injurious and unfit for consumption.

It is necessary, therefore, that the bacteria normally inhabiting milk should be destroyed, and this is most easily accomplished by boiling the milk for about five minutes, and allowing it to cool in a covered vessel. By this means all living bacteria are killed, and a medium suitable for inoculation is obtained.

The milk may then be poured into bottles or jars that have been previously cleaned with boiling water, and then allowed to drain in an inverted position. The contents of a tube of liquid culture should then be added to each pint of milk, the vessel covered and placed in a warm position, and the temperature kept at 100° to 105° F. for eight to ten hours. If the required temperature is provided the Bulgarian Bacillus rapidly multiplies, until, at the end of four to five hours, the milk has attained a creamy consistency, and is then in the best condition for administration to children, or to those who object to the acid taste of the finished product. After about eight to ten hours from the time of inoculation, the milk will be converted to a stiff mass possessing a strong pleasant acid taste.

Various forms of apparatus have been devised for maintaining a constant temperature, and wherever it is intended that a large quantity of soured milk should be prepared, the use of such an apparatus is absolutely necessary. On a small scale, however, a well insulated jar may be used, or, better still, one of the inexpensive vacuum flasks now on the maket.

How to Take Soured Milk.

Soured milk is especially palatable in summer and may be taken in a variety of ways ; the stiff curdled milk may be stirred vigorously with a spoon or glass rod, which has been previously scalded with boiling water ; the milk may then be drunk.

A second method is to spread the curdled milk on bread, either alone, or with the addition of castor sugar and cinnamon.

In Turkey the soured milk, or Yaoort, is made very thick, and is served with stewed fruit or jam.

Lastly, the milk may be added to a quantity of freshly boiled and cooled milk, and taken as a beverage.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 15th, 1911.

Sir Archibald Geikie, K.C.B., President, in the Chair.

The Croonian Lecture was delivered by Prof. T. G. Brodie, F.R.S., on "*A New Conception of the Glomerular Activity*."

All the more recent work upon the kidney has proved conclusively that Ludwig's explanation of the glomerular function, viz., that the glomerulus is a filtering mechanism, is incorrect. The structural details of this highly characteristic portion of the renal apparatus strongly suggest that in some way or other the blood pressure is made use of in the work of the glomerulus. Having excluded filtration in this connection, there is yet another way in which it could be directly utilised, viz., in setting up a pressure-head by means of which the watery part of the urine could be driven through the very long and narrow tubule. In reference to this side of its activity, it is suggested that the glomerulus be termed a "propulsor."

An approximate calculation of the pressure-head necessary to drive the fluid along the tubule during the height of activity, proves that one about equal to that present within the glomerular capillaries is required.

Evidence of the action of a high intra-tubular pressure is at once obtainable from the microscopic examination of a kidney after activity. The capsules of Bowman are greatly distended and approximately spherical in shape, the glomeruli are moderately enlarged and no longer fill the capsular spaces. The tubules are straightened out, stretched, and possess a conspicuous lumen.

All these changes are exaggerated by any procedure which favours the action of this intra-tubular pressure, such as a high arterial blood pressure, obstruction to the outflow of urine from the ureter, or the stripping of the capsule from the kidney. Further, the kidney during activity is tense and hard, and distends its capsule to the utmost.

This conception of the glomerular function affords a complete explanation of the existence of a firm and inextensible capsule surrounding the kidney, as also of such phenomena as the maximum ureter pressure, the dependence of the rate of discharge of urine from the kidney upon the general blood pressure and the degree of dilatation of the renal arterioles, &c.

Applying this theory to the study of the action of diuretics in animals in which the blood pressure has been lowered so far that propulsion can no longer occur, we obtain evidence as to the parts of the renal tubules acted upon by these different substances.

Papers were read as follows :—

"*Action of Senecio Alkaloids and the Causation of Hepatic Cirrhosis in Cattle.*" By Arthur R. Cushney, F.R.S.

Various species of Senecio (ragwort) have been shown to induce fatal poisoning in cattle and horses in South South Africa, Canada, and New Zealand. The alkaloids of one of these species were isolated by Watt, and their pharmacological examination shows that they induce the same symptoms as the entire plant. The Senecio species in this country proved non-toxic, except the common groundsel (*S. vulgaris*), and extracts from the ragwort grown in Canada, where the plant is poisonous, proved devoid of action also. This may, however, be due to the season at which the plant was gathered.

"*Note on Developmental Forms of* T. brucei (pecaudi) *in the Internal Organs, Axillary Glands, and Bone-marrow of the Gerbil.*" By G. Buchanan.

"*Preliminary Note on the Extrusion of Granules by Trypanosomes.*" By Capt. W. B. Fry.

CHEMICAL SOCIETY.

Ordinary Meeting, June 1st, 1911.

Prof. Percy F. Frankland, LLD., F.R.S., President, in the Chair.

(Concluded from p. 297).

162. "*A Copper Derivative of Quinol.*" By Hugh Vernon Thompson.

An investigation into the effect of organic oxidising agents on copper showed that a solution of *p*-benzoquinone in ethyl acetate containing traces of acetic acid readily attacks copper.

The first product of the reaction is normal copper acetate, $Cu(C_4H_6O_4),H_2O$, whilst after prolonged immersion the copper becomes coated with a crystalline deposit varying in colour from orange-red to brick-brown, and the solution also turns a red colour.

Subsequent work showed that the deposit could be obtained in crystalline pellets of a deep port-wine colour by dissolving a little *p*-benzoquinone in 30 cc. of ethyl acetate to which 4 to 5 drops (about 0·07 grm.) of glacial acetic acid had been added; in this solution thin copper foil is placed so as to be only partly immersed, and the temperature kept at 10—15° for one or two days. The substance cannot be purified by ordinary means owing to its insolubility or instability in common solvents; the mean value calculated from a series of analyses gave C = 30·61; H = 3·57; Cu = 33·16 per cent, corresponding with an empirical formula, $C_5H_7O_4Cu$.

Since the initial product in the reaction is copper acetate, it is probable that the red deposit is a molecular compound containing copper acetate, in which case the molecular formula must be at least twice the empirical formula, namely, $C_{10}H_{14}O_8Cu_2$. If we assume that this is the correct molecular formula, the composition can be expressed as (*a*) $C_6H_6O_2,CuO,Cu(C_4H_6O_4),H_2O$, or (*b*) $C_6H_6O_2Cu,Cu(C_4H_6O_4),2H_2O$.

That the substance is a molecular compound of hydrated copper acetate and a copper derivative of quinol follows from the facts that decomposition by glacial acetic acid in ether gives quinol and the salt $Cu(C_4H_6O_4),H_2O$, and that on gently heating the compound in an atmosphere of carbon dioxide *p*-benzoquinone and water are liberated, leaving a residue of metallic copper and anhydrous copper acetate.

The compound can be obtained in small amounts by other methods, but the quinol derivative has not yet been isolated from the copper acetate.

Nitric acid reacts with this compound to give a yellow crystalline substance, which is either a mixture of copper picrate and copper oxalate of approximately constant composition, or a molecular compound of the two salts of the composition $2[(C_6H_2O_7N_3)_2Cu,5H_2O],7(C_2O_4Cu,H_2O)$.

163. "*The Action of Salt Solutions and of Sea-water on Iron at various Temperatures.*" By John Albert Newton Friend and Joseph Hallam Brown.

The authors exposed thin plates of pure iron to the corrosive action of various concentrations of common salt and of sea-water at different temperatures. Below 13° it was found that dilute solutions exert a more corrosive action than distilled water at the same temperature; above 13°, on the other hand, they exert a less corrosive action. At 13° the corrosive action is practically the same for dilute solutions of common salt, for ordinary sea-water, and for distilled water. This temperature is therefore styled by the authors the "Inversion Temperature."

164. "*Some Derivatives of Gelsemine.*" By Charles Watson Moore.

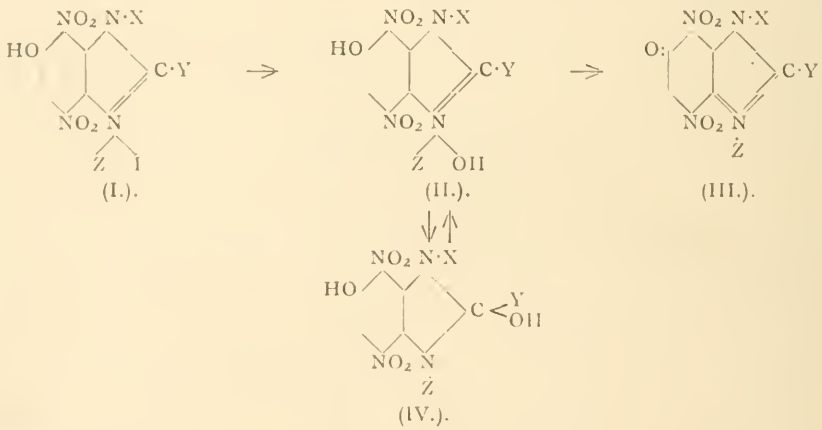
Gelsemine, $C_{20}H_{22}O_2N_2$, is stable towards alkali hydroxides and reducing agents. By treatment with oxidising agents, on the other hand, the molecule is decomposed, and no definite products have been obtained by this means.

On boiling gelsemine with concentrated hydrochloric acid for some hours, three new bases are formed, which have been designated as apo*gelsemine*, isoapo*gelsemine*, and *chloro*-isoapo*gelsemine*. Of these, apo*gelsemine*, $C_{20}H_{24}O_3N_2$, is the chief product of the reaction, and although it cannot be crystallised, it yields well characterised crystalline derivatives. Chloro-*isoapo*gelsemine, $C_{20}H_{23}O_2N_2Cl$,, and its hydrolytic product, *isoapo*gelsemine, $C_{20}H_{24}O_3N_2$, are only formed in relatively small amounts. Both these bases crystallise readily, and they, and several of their derivatives, have been characterised.

It has also been observed that when *Gelsemine methyl hydroxide* is heated at 200° in aqueous solution, the expected gelsemethine is not produced, the methyl hydroxide losing methyl alcohol with regeneration of gelsemine.

165. "*Synthesis with Phenol Derivatives containing a Mobile Nitro-group.* Part IV. *Quinone-imides, Asymmetric Quaternary Ammonium Compounds, and Asymmetric Carbinols.*" By RAPHAEL MELDOLA and HAROLD KUNTZEN.

Setting out from the iminazoles obtained by the action of primary amines on trinitroacetylaminophenol, it was shown that iminazolium iodides (I.) can be obtained by heating the iminazoles with alkyl iodides, the resulting compounds being hydrolysable with the formation of the iminazolium hydroxides (II.). The latter, on heating, lose water, and pass into quinone-imides (III.), and on solution in alkali are transformed into the isomeric carbinols (IV.).



It was pointed out that compounds of the types I. and II. contain an asymmetric nitrogen atom of the form O:N *a b c*, and should therefore be resolvable into optically active antipodes. The carbinol form (IV.) also contains an asymmetric carbon atom, and should be resolvable. As the carbinols and iminazolium hydroxides are interconvertible, the interesting possibility is thus offered of transferring optical activity from a nitrogen to a carbon atom. Type III. represents a new class of quinone-imide derivatives, for which the authors propose the name of *iminazolones*. The carbinols (IV.) are named, in accordance with precedent, *iminazolols*. Several compounds of each series were described.

166. "*Note on a Colour Change in β-Paranitrophenol brought about by Sunlight.*" By THOMAS VIPOND BARKER.

p-Nitrophenol yields two modifications which have been examined crystallographically by the author (*Zeit. Kryst. Min.*, 1907, xliv., 159). The two modifications possess great similarity in the values of their prism angles; that they are quite distinct, however, follows from the observed transformation of one into the other on heating under the microscope. The transition temperature, if one really exists, has not been accurately determined, but the author's observations would seem to point to a temperature of 63°, for a saturated toluene solution yields crystals of either modification according as the temperature is above or below 63°. That modification which appears at high temperatures will henceforth be termed α, the other β.

The α-modification is almost colourless, being of a very pale lemon-yellow tint. The β-modification, on the other hand, is of a pronounced yellow colour; but on allowing it to remain for some time the crystals were found to acquire gradually a red tinge on the surface. The α-crystals, on the other hand, preserved their original tint.

Experiments were therefore made under varying conditions, and it was soon found that the red coloration appears only when the crystals are exposed to sunlight. The brighter the light the quicker is the change; in dull weather crystals may be exposed for many days without any appreciable change, whilst on a bright day the red coloration is apparent after an hour or so. Absolutely no change takes place if the crystal be kept in the dark. A tube which has been kept wrapped up in black paper presents no trace of change, even after a lapse of seven years.

It was at first thought that the coloration might possibly be due to the formation of an ammonium salt. That this is not the case is proved by the fact that the change proceeds in a desiccator over sulphuric acid, and again when the desiccator is filled with hydrogen or carbon dioxide. The change, although quickly enough detected by the eye, must in reality be a very slow process, since crystals after some months' exposure still present a yellow nucleus, and it is likely that the red material acts as a protection against further change by absorbing the actinic rays.

It is very remarkable that the α-modification is wholly unacted on. Of this there can be no doubt, as the following will show. Solutions in water at the ordinary temperature yield crystals, the great majority of which are those of the β-modification, but, in addition, some crystals of the α-modification also appear. Owing to the similarity in habit, it is often impossible without an actual measurement on the goniometer to distinguish between crystals of the two modifications. The whole of one crop thus obtained was collected into a tube, and exposed to sunlight for some time; all the crystals with the exception of two turned red after a few hours. The action was allowed to proceed for a few months; but even after this prolonged treatment the two crystals still failed to show the slightest trace of change. They were therefore taken out, and measured on the goniometer, and proved to be crystals of the α-modification. A few of the red crystals selected at random proved on measurement to be those of the β-modification.

Commercial *p*-nitrophenol consists of a mixture of both

kinds of crystals, and on examination it will generally be found that some are red whilst others are not. The former are those of the β-modification.

Cases of colour change have previously been observed, but as far as the author is aware, no case has previously been discovered in which the change is restricted to one crystalline modification. At present the usually accepted view with regard to polymorphous modifications is that the difference in crystalline form is not due to a difference in the chemical molecule, but rather in the different mode of packing of the molecules. The above remarkable difference of behaviour, however, of the two "polymorphous" modifications of *p*-nitrophenol would seem to argue for a difference in chemical structure; it is difficult to see how a mere difference in the arrangement of the same chemical molecules should render one crystal structure immune to the action of actinic rays. It is therefore suggested that the chemical structures of the α- and β-modifications of *p*-nitrophenol are different.

167. "*The Sensitiveness of Pentamminenitrosocobalt Salts to Light.*" By Oskar Krafft Heinrich Burger.

In purifying the red variety of pentamminenitrosocobalt nitrate (Sand and Genssler, *Ber.*, 1903, xxxvi., 2083; *Annalen*, 1903, cccxxix., 194) by crystallisation from water, it was noticed that the deep red solution is sensitive to light, and is slowly decomposed with the formation of nitric oxide and a green flocculent precipitate of cobaltous hydroxide. This decomposition cannot well be explained but by the assumption that the red salt changes under the influence of light into the black isomeride considered, by Sand and Genssler, to contain bivalent cobalt, and that the latter is then decomposed by the water. The reaction may be represented by the equation—

$$Co_2(N_2O_2)(NH_3)_{10}(NO_3)_4 + H_2O = \\ = Co(OH)_2 + 2NO + 4NH_4NO_3 + 6NH_3.$$

If the solution is kept acid during the decomposition, the same quantity of gas is developed, but no precipitate is formed, the cobalt remaining in solution as cobaltous salt.

A similar decomposition is observed when a solution of the red salt is heated for some time. The development of gas is the same, but instead of the green flocculent hydroxide a more compact black cobaltous oxide is formed. That the decomposition in light is really due to the rays of light, and not to those of heat, is shown conclusively by the fact that the more refrangible end of the spectrum only produces the reaction.

A determination of the solubility in water of the red nitrate showed that one part of the salt dissolves in about twenty-five parts of water. For the purpose of identifying the gas evolved in the reaction, a few cc. of an acidified solution of the red nitrate were placed on top of the mercury in a eudiometer, and subjected for several hours to the action of direct sunlight. It was found advantageous to have the solution acidified, because otherwise the gas bubbles become attached to the flocculent precipitate, and do not separate easily. The acid merely serves to prevent the formation of cobaltous hydroxide, otherwise the reaction proceeds in exactly the same way. The slow liberation of gas was the only sign of the change taking place. No variation of colour could be observed, as the colour of the red cobaltic nitrate in solution is almost the same as that of a cobaltous salt. The gas evolved was proved to be nitric oxide.

The following short account of a series of experiments will give an idea of the velocity of the reaction. Four flat porcelain dishes of about 8 cm. diameter were charged with 10 cc. each of a solution containing 1·620 grms. of the red nitrate per 100 cc. They were all exposed at the same time to direct sunlight (the sun being close to the zenith), and successively withdrawn at intervals of five minutes. The precipitate formed was collected in the dark, the filtrate evaporated with sulphuric acid, and the cobalt sulphate weighed.

	Grm. of nitrate.
10 cc. of the original solution contained ..	0·1620
10 cc. contained after 5 minutes exposure	0·0988
,, 10 ,,	0·0828
,, 15 ,,	0·0704
,, 10 ,,	0·0698

It is evident that the reaction slows down as the solution becomes more dilute, and the soluble products of the reaction (ammonia and ammonium nitrate) accumulate in the solution.

The spectrum of the red solution shows only general absorption of the more refrangible part from the green onwards. As would be expected, only those rays that are absorbed will produce decomposition. Solutions of the red nitrate of equal strength were exposed to sunlight covered with red, yellow, green, and blue glasses respectively. After several days' exposure, the solution under the red and yellow glass did not show any sign of decomposition, that under the green filter only a slight one, whereas the solution under the blue glass was decomposed to a considerable extent.

It was suggested that the solution of the red nitrate might be used with advantage for the construction of a chemical photometer.

168. "*Lecture Experiment to Illustrate Dust Explosions. The Surface Areas of certain Finely-divided Combustible Solids.*" By William Robert Lang and Hoyes Lloyd.

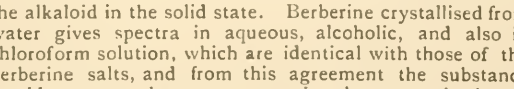
The following experiment serves as an illustration of the liability to explosion of the dust from starch and from coal when mixed with air. A glass cylinder, about seven feet long and four inches wide and open at both ends, is set up vertically, wires from an induction-coil being led through glass tubes into the middle of the chamber. Lycopodium, starch, and coal-dust, when allowed to fall into the tube and a spark passed through the mixture, ignite with explosive violence, the combustion being propagated throughout the length of the tube, and the flames issuing a considerable distance from either end Direct application of a lighted taper produces the same result.

With the view of arriving at some approximate idea of the total surface of the combustible matter exposed to the air in such cases, the dimensions of the particles of the substances employed were ascertained by a microscopic examination, and the surface-area per 100 grms. of each calculated. In like manner, "pyrophoric carbon" and pyrophoric iron were examined, and similar calculations made. The results may be summarised as follows:—

Substance.	Mean diameter of particles. Mm.	Total surface area for 100 grms. of substance. Square metres.
Lycopodium	0·028	20·92
Maize starch	0·0122	32·78
Coal-dust (*a.* Medium	0·012	33·33
Coal-dust (*b.* Fine ..	0·0016	250·00
"Pyrophoric carbon" ..	0·00125	332·00
Pyrophoric iron	0·0054	15·08

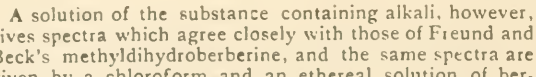
169. "*The Constitution of Berberine.*" By Charles Kenneth Tinkler.

From an examination of the ultra-violet absorption spectra of berberine and its simple derivatives, evidence has been obtained of the existence of two modifications of the alkaloid in the solid state. Berberine crystallised from water gives spectra in aqueous, alcoholic, and also in chloroform solution, which are identical with those of the berberine salts, and from this agreement the substance would appear to have an ammonium-base constitution as represented by Formula I. (compare Perkin, *Trans.*, 1910, xcvii., 321):—



I.

A solution of the substance containing alkali, however, gives spectra which agree closely with those of Freund and Beck's methyldihydroberberine, and the same spectra are given by a chloroform and an ethereal solution of berberinal, the substance precipitated by the addition of sodium hydroxide to an aqueous solution of berberinium hydroxide. This agreement can only be explained by assigning to berberinal the carbinol Formula II., and the name *berberinol* is suggested for this substance :—



II.

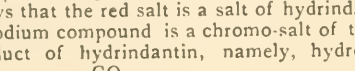
The transformation of berberinol into berberinium hydroxide is readily followed by means of the spectroscope.

Spectroscopic evidence was also obtained in support of the view that the products of decomposition of berberinol by excess of alkali are dihydroberberine and oxyberberine.

Since both modifications of the alkaloid can be obtained in solution in chloroform, it appears that both the ammonium base and the carbinol exist in the solid state. In this respect berberine differs from the other substances that have been investigated in connection with the carbinol—ammonium base—aldehydeamine isomerism, in which cases evidence of the existence of the carbinol form alone in the solid state has been obtained.

170. "*Triketohydrindene Hydrate.* Part IV. *Hydrindantin and its Analogues.*" By SIEGFRIED RUHEMANN.

Hydrindantin has been shown to yield a red solution with sodium carbonate and a blue solution with sodium hydroxide (*Trans.*, 1911, xcix., 792). An examination of these shows that the red salt is a salt of hydrindantin, and the blue sodium compound is a chromo-salt of the hydrolytic product of hydrindantin, namely, hydroxydiketohydrindene, $C_6H_4<^{CO}_{CO}>CH\cdot OH$. This substance, which is to be regarded as the analogue of dialuric acid, could not be obtained pure, because it is readily oxidised to hydrindantin. Owing to the close resemblance of hydrindantin to alloxantin, the violet barium compound which this substance yields with baryta is to be regarded as a chromo-salt of dialuric acid, instead of alloxantin. The author also considers that isatide is an analogue of alloxantin, and that, therefore, it must be represented thus :—



(compare Heller, *Ber.*, 1904, xxxvii., 946). Further, it was found that dialuric acid does not unite with diketohydrindene hydrate to form an analogue of alloxantin, but that the acid reduces the triketone to hydrindantin. This substance is also produced from oximinodiketohydrindene, $C_6H_4<^{CO}_{CO}>C:NOH$, by means of concentrated hydriodic acid ; on using stannous chloride, instead of hydriodic acid, the analogue of uramil, namely, diketohydrindamine, $C_6H_4<^{CO}_{CO}>CH\cdot NH_2$, is formed.

171. "*Aminoquercetin.*" (Preliminary Note). By EDWIN ROY WATSON.

An *aminoquercetin* has been obtained from quercetin by completely methylating to protect the molecule, nitrating, reducing, and demethylating.

Nitropentamethylquercetin, $C_{15}H_4O_2(OMe)_5\cdot NO_2$, prepared by dissolving pentamethylquercetin in cold nitric acid (D 1·4), crystallises from acetone in bright yellow needle-shaped crystals, melting at 202—204°.

Aminopentamethylquercetin, $C_{15}H_4O_2(OMe)_5\cdot NH_2$, prepared by reducing the nitro-compound with tin and alcoholic hydrochloric acid, crystallises from benzene in almost white stout prisms, melting at 200—202°. Its *hydrochloride* crystallises from dilute hydrochloric acid in white needle-shaped crystals, and its *sulphate* from dilute sulphuric acid also in white needle-shaped crystals. An *acetyl* derivative crystallises from alcohol and acetic acid in stout white prisms, melting at about 223—226°.

Aminoquercetin, $C_{15}H_4O_2(OH)_5\cdot NH_2$, is obtained in solution as hydriodide on boiling either aminopentamethylquercetin or nitropentamethylquercetin with hydriodic acid (D 1·7). The free base is isolated in light yellow needle-shaped crystals by decomposing its salts with pyridine and water. The *hydrochloride*, $C_{15}H_{11}O_7N,HCl$, crystallises from dilute hydrochloric acid in yellow fine needle-shaped crystals, the *hydriodide* from dilute hydriodic acid in orange-coloured warts, and the *sulphate* from dilute sulphuric acid in yellowish brown warts. An *acetyl* derivative, crystallising from alcohol and acetic acid in white rhombs, melting at 151—153°, is obtained by acetylation of either aminoquercetin or its salts ; it is either the hexa- or the hepta-acetyl derivative.

Aminoquercetin dyes mordanted wool the following shades :—Brown on chrome, yellow-brown on alum, orange-red on tin, and brownish-black on iron. The shades are browner and deeper than corresponding dyeings with quercetin.

In the course of this investigation, the following quercetin derivatives have also been prepared.

Pentamethylquercetin hydrochloride, $C_{20}H_{20}O_7,HCl$, *hydrobromide*, $C_{20}H_{20}O_7,HBr$, *sulphate*, $C_{20}H_{20}O_7,H_2SO_4$, and *nitrate*, $C_{20}H_{20}O_7,HNO_3$. The first three of these oxonium salts are obtained in bright yellow needle-shaped crystals on adding a concentrated solution of the corresponding acid to a solution of pentamethylquercetin in glacial acetic acid, and the nitrate is obtained, also in bright yellow needles, by adding concentrated nitric acid to a solution of pentamethylquercetin in absolute alcohol.

Trinitropentamethylquercetin, $C_{15}H_2O_2(OMe)_5(NO_2)_3$, prepared by dissolving pentamethylquercetin in cold fuming nitric acid, is a canary-yellow substance, melting at 190—205°.

Dibromopentamethylquercetin, $C_{15}H_3O_2Br_2(OMe)_5$, prepared by brominating pentamethylquercetin in glacial acetic acid solution, crystallises from alcohol or benzene in white short prisms or leaflets arranged in sheaves, melting at 173—175°.

Dibromopentamethylquercetin hydrobromide,

$$C_{20}H_{18}O_7Br_2,HBr,$$

is obtained in bright yellow needle-shaped crystals as an intermediate compound in the bromination of pentamethylquercetin.

Dibromonitropentamethylquercetin,

$$C_{15}H_2O_2Br_2(OMe)_5\cdot NO_2,$$

prepared by dissolving dibromopentamethylquercetin in cold nitric acid (D 1·4), crystallises from alcohol or acetone in light yellow rhombs, melting at 173—175°.

Pentamethylquercetindiazonium chloride,

$$C_{15}H_4O_2(OMe)_5\cdot N_2Cl,$$

is obtained in bright yellow needle-shaped crystals on diazotising aminopentamethylquercetin hydrochloride.

Pentamethylquercetindiazonium sulphate separates in yellow needle-shaped crystals on adding dilute sulphuric acid to a cold saturated aqueous solution of the corresponding diazonium chloride.

Pentamethylquercetinazo-β-naphthol,

$$C_{15}H_4O_2(OMe)_5\cdot N_2\cdot C_{10}H_6\cdot OH,$$

prepared by mixing an alkaline solution of β-naphthol and a solution of pentamethylquercetindiazonium chloride, crystallises from glacial acetic acid in deep crimson needle-shaped crystals, melting and decomposing at 211°.

The amino-group in aminoquercetin is probably in the catechol nucleus in that position which is para- with respect to one of the hydroxyl groups and meta- to the other, but experiments are in hand to determine its position definitely. Experiments are also in progress to convert

aminoquercetin into the corresponding hydroxyquercetin, and from the compounds now described to prepare other derivatives with dyeing properties.

172. "*The Reduction of Nitroacenaphthene.*" By Holland Crompton and Maggie Walker.

The methods suggested by Quincke (*Ber.*, 1888, xxi., 1454) and by Graebe (*Annalen*, 1903, cccxxvii., 81) for the reduction of nitroacenaphthene are slow, and were not found to give good yields of aminoacenaphthene. Better results were obtained on using zinc dust and water as a reducing agent.

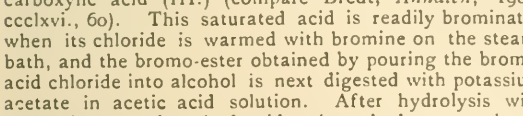
Nitroacenaphthene is mixed intimately with about five times its weight of zinc dust, and sufficient water is added to form a thin paste. The mixture is heated for ten hours on a water-bath, then dried at about 60°, and extracted with light petroleum. The aminoacenaphthene obtained on distilling off the solvent is slightly brown, owing to the presence of a small quantity of a brown coloured by-product, which has not been further examined. It can be purified by treatment with dilute sulphuric acid. It is best to crystallise out the sulphate, as this salt is more stable on exposure to air than is the free base. The yield in the above process is about 60 per cent of the theoretical.

173. "*Epicamphor: a New Isomeride of Camphor.*" (Preliminary Note). By Frederick Russell Lankshear and William Henry Perkin, jun.

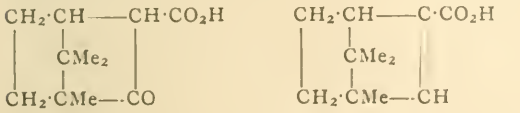
Two keto-derivatives should be obtainable from camphane, namely,—

Camphor. Epicamphor.

and of these the second, for which the name *epicamphor* is proposed, has not yet been described. Owing to the interest attaching to this substance one of the authors has for some years attempted to prepare it, but, until recently, without success. It may be obtained by the following series of reactions:—Camphorcarboxylic acid (I.) is converted by reduction and subsequent elimination of water into bornylenecarboxylic acid (II.), and the authors have observed that this acid is converted by reduction with palladium and hydrogen quantitatively into camphanecarboxylic acid (III.) (compare Bredt, *Annalen*, 1909, cccl xvi., 60). This saturated acid is readily brominated when its chloride is warmed with bromine on the steam-bath, and the bromo-ester obtained by pouring the bromo-acid chloride into alcohol is next digested with potassium acetate in acetic acid solution. After hydrolysis with alcoholic potassium hydroxide, the α hydroxycamphanecarboxylic acid (IV.) is oxidised by lead peroxide, permanganate, or also by chromic acid, and, in each case, small yields of epicamphor are obtained.



(I.). (II.).



(III.). (IV.).

Epicamphor is readily volatile in steam, has the same odour as camphor, and is remarkably like this substance in almost all its properties; it melts at about 165°, but this melting-point, as well as the others mentioned in this paper, will be carefully revised when larger quantities of material are available.

Found, C = 78·3; H = 10·5. $C_{10}H_{16}O$ requires C = 79·0; H = 10·4 per cent.

Epicamphoroxime melts at about 102°, and has the same odour as camphoroxime, which melts at 119°. (Found, C = 72·3; H = 10·4; N = 8·6. $C_{10}H_{17}ON$ requires C = 71·8; H = 10·2; N = 8·4 per cent). *Epicamphorsemicarbazone* separates from benzene in flocks and from methyl alcohol in glistening needles, and melts at 225—227° with effervescence, whereas camphorsemicarbazone melts at 236—258°. (Found, N = 20·1. $C_{11}H_{19}ON_3$ requires N = 20·1 per cent).

The authors intend to prepare a number of derivatives of epicamphor with the object of comparing them with the corresponding derivatives of camphor.

PHYSICAL SOCIETY.

Ordinary Meeting, June 9th, 1911.

Prof. H. L. Callendar, F.R.S., in the Chair.

A paper on "*The Lüders' Lines on Mild Steel*" was read by Mr. W. Mason.

Previous investigations have shown that Lüders' lines on specimens of mild steel and wrought iron, strained in tension, are inclined at about 50° to the axis of pull. For tests in compression the information available is not precise, and though the angle of the lines with the direction of the compression is commonly understood to be about 40°, some doubt has been thrown on this point.

The author had found previously that the lines are well developed on the surface of mild steel tubes. Since it was easy to obtain a compressive stress of practically uniform distribution in tubes under end pressure, while at the same time a hoop tensile stress could be induced by internal fluid pressure, the author confined his attention to the lines on tubular specimens. These were of mild steel, either hot or cold drawn, and most of them were annealed. They varied in bore from 2¾ in. to 3 in., and in thickness of wall from about 0·08 in. to 0·125 in. Four sets of tubes were tested under end loading, simultaneously (for the most part) with internal water pressure, these loadings being so arranged as to give at the yield point ratios of the longitudinal compressive stress to hoop tensile stress ranging from 0·25 to ∞.

The Lüders' lines on the outer surface appeared at the yield point indicated by the extensometer—*i.e.*, their appearance coincided with the commencement of the large "yield" strain. In all cases where there were lines on the inner and outer surfaces of a tube, an inner and outer line, and also the ends of these lines, were found to be radially opposite; showing that the lines were traces of surfaces or canals of disturbance which passed through the tube wall, and indicating, moreover, that the disturbance spread spirally onwards, and not outwardly from a line initially formed on the more severely stressed inner surface.

The inclination α of the lines to the axis of the tube was found to vary in the following way for tubes under end load and internal pressure:—

For $\frac{\text{longitudinal stress}}{\text{hoop stress}} = 0{\cdot}25$, $\alpha = 42°$ (about).

" " $= 1$, $\alpha = 45°$ (about).

" longitudinal stress only, $\alpha = 50°$ (about).

For values between 0·25 and 1, and between 1 and ∞ α became progressively larger.

Some tests of tubes under external water pressure and longitudinal tension gave results similar to those above mentioned. The directions of the lines with respect to the axes of like stress were practically the same, though the inclinations to the axes of the tubes were now complementary to the values of α quoted above.

The conclusion is drawn that the Lüders' surfaces have the same, or approximately the same, inclination to an axis of simple pull or simple push. With stresses of opposite sign at right angles to each other the lines and surfaces are more inclined to the stress of greater intensity, and with equal intensities the surfaces are at about 45°. The author suggests that if a shear stress of given intensity be the only condition for that spreading of plastic strain which commences at the yield point, then there is no reason why there should be any variation in the angle of the Lüders' lines and surfaces. The variation suggests that not only the maximum shear stress—*i.e.*, the half difference of the greatest and least principal stresses—but also the magnitudes of the principal stresses are factors in producing the yielding condition in mild steel.

Dr. Chree said Lüders' lines seemed to possess a double interest. If their first existence coincided in time with the ending of linearity in the stress-strain relation, their presence intimated that the ordinary mathematical equations had ceased to apply. In this connection their utility would be greater if the stress function supposed to determine the elastic limit were greatest at a point or small area visible to the eye, instead of, as in the present case, over the whole inner surface of a cylinder. The phenomenon seemed, however, also interesting in itself. The nature of the change in the material and the mode of propagation of the altered volume would be more easily studied if the altered material could be recognised in sections of the cylinders.

Prof. Coker asked whether the lines were a surface phenomenon produced by the stresses in the oxide.

Prof. C. A. M. Smith pointed out that slipping in the material takes place in a definite manner even after quite a long time, and that the lines might be due to this.

Mr. E. H. Rayner pointed out that the elastic constants in the two directions would probably be different, and that the compression might put on shear resulting in lines only appearing in one direction.

Dr. A. Russell asked the author if his results threw any light upon the phenomena obtained when wires are drawn.

Mr. Maclachan asked the author if he had ever tried polishing the surface of his tubes. His own experiments made on the compression of solids showed that the lines were not always spiral, but approximated to a section of the cylinder made by a plane inclined at 45°.

The Author, in reply, stated that he did not know whether the lines occurred at the elastic limit or just after. The lines were not a surface phenomenon, as they were obviously related to the bend in the stress-strain diagram. Mr. Rayner's difficulty was got over by reversing the stresses. The lines were not due to massive slipping, but to the propagation of a disturbance.

A paper on "*A New Method of Harmonic Analysis by Averaging Selected Ordinates*" was read by Prof. S. P. Thompson.

Assume with Fourier that the curve representing any periodic single-valued function of x may be expresssd by the harmonic series—

$$y = A_1 \sin x + A_2 \sin 2x + A_3 \sin 3x + \ldots\ldots + B_1 \cos x + B_2 \cos 2x + B_3 \cos 3x.$$

Then to find the coefficient of any term, A_n or B_n, it suffices—subject to a limitation stated below—to measure off on the curve $2n$ equidistant ordinates over one period; that is, spaced at successive intervals apart of π/n. Then, having reversed the sign of every alternate ordinate, the simple algebraic mean of them gives the coefficient sought. For cosine-coefficients the first ordinate must be taken at the origin; while for sine-coefficients the first ordinate must be taken at a point $\frac{1}{2}\frac{\pi}{n}$ from the origin. In symbols this is—

$$A_n = \frac{1}{2n}\left(y_{\frac{1}{2}\pi/n} - y_{\frac{3}{2}\pi/n} + y_{\frac{5}{2}\pi/n} - y_{\frac{7}{2}\pi/n} + \ldots - y_{\frac{4n-1}{2}\pi/n} \right);$$

$$B_n = \frac{1}{2n}\left(y_0 \quad - y_{\pi/n} + y_{2\pi/n} - y_{3\pi/n} + \ldots - y_{(2n-1)\pi/n} \right)$$

The limitation is that if, in finding the nth harmonic, there be present also the $3n$th, or the $5n$th, or the $7n$th, &c., these will be included in the average found by the process, and must, if present, be separately determined and eliminated.

The process is much facilitated by the use of templates of transparent celluloid having equispaced vertical lines engraved upon them. They are laid down on the curve, and the values of the selected ordinates are thus readily measured off. For analysis of valve-motions, of alternating-current curves, of tidal observations, and diurnal magnetic variations, the method presents certain advantages, as it requires no multiplication of ordinates by sines or cosines.

The President commented upon the extreme ease with which the method adapted itself to the analysis of experimental curves.

Dr. Russell remarked that the method can be usefully employed in interpolation as well as in harmonic analysis. In this connection he gave a brief *résumé* of Gauss's extension of Lagrange's interpolation formula. He also pointed out certain cases in which Fourier's analysis fails to be of practical use.

Sir G. H. Darwin has communicated the following remarks:—In 1874 Mr. Archibald Smith published in the Admiralty Scientific Manual on "Deviations of the Compass," schedules whereby the multiplications in the usually accepted process are simple. This same arrangement has been in use for the harmonic analysis of tides since 1870, and in his "Manual of Tidal Observations," Major Baird gave multiplication tables for the sines of 15°, 45°, 60°, 75°, which render this part of the work so easy that avoidance of all multiplication hardly seems necessary. In 1884, in "Tables and Formulæ to Facilitate the Computation of Harmonic Coefficients," General Sir Richard Strachey gave rules which reduce the multiplications still further. In both these schemes Prof. Thompson's principle is used for some of the higher harmonics. Smith's and Strachey's schedules are arranged for twenty-four hourly values, but they may be equally well used for twelve ordinates. Schedules for the use of any other number of ordinates would have to be prepared specially, and in such cases Prof. Thompson's rules might prove very convenient.

A Demonstration of the Subjective Nature of the Difference Tone was given by Prof S. P. Thompson.

Two tuning forks of frequencies 3328 and 3584 were sounded loudly. On striking the second the difference tone was heard, but while the notes from the two forks seemed to come in a definite direction from an external source the difference tone seemed to be located in the ear itself.

A Demonstration of Spinning Tops and Gyroscopic Apparatus was given by Sir George Greenhill.

A 52 in. Otto bicycle wheel was shown mounted on an axle with ball bearings, and spun by hand with the point in a small cup, to serve as a spinning top visible to a large audience.

The gyroscopic apparatus was made of an ordinary 28 in. bicycle wheel, the axle screwed into a stalk of a short length of rifle barrel, suspended from a lug on a bicycle hub; the hub is fastened to an iron bracket, which is bolted to the under side of a beam or sleeper, large enough to absorb vibration and resting on two step ladders.

The wheel is spun by hand, and the axle is projected to obtain any desired gyroscopic motion, undulating, looped, or with cusps.

The wheel can be detached by unscrewing the pin through the lug, and can then be used like the large wheel as a spinning top, or as the "Top on the top of a Top," described in Maxwell's "Life."

Put the wheel out of balance by a bar through the spoke and hold the axle, and it will serve as a pendulum, making oscillations however large, or complete revolutions; and the effect may be investigated of varying the angle of the axle with the vertical.

A Model Illustrating the Passage of a Light Wave through Quartz, constructed by Prof. H. N. Allen, of Poona, was described by Dr. H. S. Allen.

If a crystal is so cut, and a wave sent through it in such a way as to avoid separation of the two component waves by double refraction, it is easy to construct models showing how a vibration gradually alters in form as it passes through the crystal. The model exhibited illustrates the passage of a wave originally plane polarised through a crystal which rotates the plane of polarisation of light sent along its axis (quartz). The direction of propagation is oblique to the axis of the crystal. It is assumed that the crystal has been cut so that the surface of incidence is perpendicular to the direction of propagation of the wave. As the wave progresses the linear vibration opens out into a counter clockwise elliptical one, while the major axis of this ellipse rotates in the counter-clockwise direction. The minimum ratio between the axes is reached when the retardation is half a period. A retardation of a whole period gives a linear vibration again, and so on. If the model is cut by a series of parallel planes the sections give the form of the elliptic vibration as the wave travels through the crystal. The instantaneous wave forms can be drawn on the surface of the model.

A paper on "*The Measurement of Contact Differences of Potential*," by Prof. A. Anderson and Mr. J. E. Bowen, was taken as read.

The paper describes two methods of measuring the contact differences of potential of pairs of metals. The first, or deflection, method depends on the property which a radio-active source has of destroying a field of electrostatic force in air, and the second, or null, method on the possibility of determining by means of such a source whether such a field exists between two plates at zero potential. Measurements were made on ten different metals, and it was found that both methods gave practically the same results provided that the time which was allowed to elapse between the two measurements was sufficiently small. The latter law was verified.

A paper entitled "*A Short Table of Circular and Hyperbolic Functions for Complex Values of the Argument*," by Mr. A. Johnstone, was also taken as read.

NOTICES OF BOOKS.

Elementary Chemistry for Coal-mining Students. By L. T. O'Shea, M.Sc. (Sheffield), B.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911. (6s. net).

The author's experience in lecturing to students and others connected with the coal-mining industry has enabled him to make on the whole a very judicious choice of material for inclusion in this text-book, although he has perhaps taken rather an unduly liberal view of the amount of theoretical knowledge which his readers should possess. In the introduction the general principles of chemistry are explained in a necessarily very condensed form, which, however, will no doubt answer the purpose for which it is designed, and then the study of the atmosphere, water, hydrogen, &c., is taken up, special references being made to any problems that are of importance in mining. Thus a whole chapter is devoted to gas and atmospheric pressure. The elements sulphur and carbon are considered in detail and a chapter is given to a discussion of the Atomic Theory. The structure and properties of flames and the construction of modern safety lamps are well treated, and the last chapters deal with the chemistry of coal, the nature and use of explosives, and the causes and prevention of explosions in mines. This part of the book is intended more particularly for mine managers, who should be thoroughly conversant with all that the author has to say upon these highly important subjects. The book certainly does not err upon the side of incompleteness, and it will be found of real practical use to technical students and colliery officials.

Alcoholic Fermentation. By Arthur Harden, Ph.D., D.Sc., F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911. (4s. net).

This book is based upon courses of lectures given at London University and the Royal Institution in the years 1909 and 1910, in which the problem of the nature of alcoholic fermentation was discussed in the light of Buchner's discovery of zymase. The history of research work on fermentation previous to Buchner's discovery is treated in the introductory chapter, in which a very lucid account is to be found of the essentials of earlier important theories. Then the preparation of zymase and practical methods of studying its properties and action are discussed, and a chapter is given to the consideration of the author's discovery of the function of phosphates in alcoholic fermentation; in this connection Iwanoff's theory is shortly alluded to in a very fair spirit. Recent investigations of the function of the co-enzyme of yeast and its chemical nature are well summarised, and the concluding chapters deal with the action of retarding and accelerating agents on the enzyme of yeast-juice, the by-products of fermentation, and the chemical changes involved in the phenomenon.

Modern Methods of Sewage Purification. By G. Bertram Kershaw. London: Charles Griffin and Co., Ltd. 1911. (21s. net).

The problem of the best methods of designing and maintaining sewage works so as to obtain the maximum of efficiency at the minimum cost is discussed in a thoroughly practical spirit in this treatise. The author, who for twelve years acted as engineer to the Royal Commission on Sewage Disposal, has a unique knowledge of the factors to be taken into consideration before adopting any particular method, and by his admirable classifications and tabulations he places his information at the disposal of the public in the most convenient and convincing form. The subject is treated mainly from the practical and engineering point of view, and special stress is laid upon financial considerations and methods of lowering the cost of the disposal of sewage; thus the suitability of different crops for growing on a sewage farm is treated in some detail. The book is excellently indexed and provided with an abundance of illustrative diagrams and plates.

Allen's Commercial Organic Analysis. Volume IV. Fourth Edition. London: J. and A. Churchill. 1911. (21s. net).

Volume IV. of the new edition of "Allen's Text-book of Commercial Organic Analysis" has been edited by Messrs. Davis and Sadtler. It deals with the properties and the methods of analytical examination of resins, rubber, and rubber substitutes and the essential oils. The list of the writers of the several sections includes the names of distinguished experts, and guarantees the authoritative nature of the contents. In the case of each substance the physical properties are admirably discussed, and some account is given of physiological properties besides methods of examination for adulterations and impurities, and an excellent table is appended of the chief sources, characteristics, and constituents of the essential oils.

Report of The Chemist for 1910. By H. W. Wiley. Washington: Government Printing Office. 1910.

The Report of the Chemist of the work done by the Bureau of Chemistry of the U.S. Department of Agriculture during the year ending June, 1910, will repay the careful study of analytical chemists in this country, for it contains many important results relating to food and drug

analysis, as well as reports of some special investigations in physiological chemistry and microchemistry. The work planned for the current year is summarised, and includes the special examination of shipments of bleached flour, of milk, and the study of fruit juices and of canned goods, besides the general routine work in each laboratory.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cliii., No. 18, May 1, 1911.

Determinations of Size of Molecules.—Jean Perrin.—To determine the magnitude of molecules Townsend and J. J. Thomson investigated the charge on the microscopic particles in suspension in a gas. The values obtained varied between 2×10^{-10} and 6×10^{-10} C.G.S. units. More recent results are $3{\cdot}1\times10^{-10}$, $4{\cdot}06\times10^{-10}$, $4{\cdot}7\times10^{-10}$. Ehrenhaft, working with dusts (obtained by sparking between metals) arrived at very discrepant results, and Millikan, from drops (obtained by pulverising a liquid) got $4{\cdot}9\times10^{-10}$. Rutherford from the number of positive projectiles forming the α-rays of radio-active substances obtained $4{\cdot}65\times10^{-10}$, while the study of the Brownian movement gives the value $4{\cdot}1\times10^{-10}$.

Molecular Weight of Uranous Oxide.—Œchsner de Coninck.—Five determinations of the molecular weight of uranous oxide, obtained by reducing uranic hydrate, $UO_3.H_2O$, by pure dry hydrogen at a red-heat, gave as a mean 270·66, the theoretical molecular weight of UO_2 being 270 5. By the reduction of uranyl chloride 270·07 is obtained.

Berichte der Deutschen Chemischen Gesellshaft. Vol. xliii., No. 6, 1911.

4-Nitroresorcin.—H. Kauffmann and W. Kugel.—The nitro derivatives of dibasic phenols can be obtained by preparing their monobenzoates and then nitrating them. When resorcin monobenzoate is nitrated two isomeric nitro monobenzoates are obtained; they both give on saponification the same nitroresorcin, which has undoubtedly the constitution $OH:OH:NO_2,1:3:4$. It forms lemon-coloured crystals which melt at 122°.

New Series of Aromatic Sulphur Compounds.—Th. Zincke.—When chlorine acts on the benzyl ethers of the mercaptans, benzal chloride is split off and sulphur compounds of the formula Ar.S.Cl. are obtained. The same compounds can be prepared by the action of chlorine on the mercaptans or the disulphides. The corresponding bromine compounds are much more difficult to prepare, although the author has succeeded in obtaining them from the nitrosulphides of benzene and toluene. The chlorine compounds can readily be converted into disulphides.

Thermic Formation of Manganates.—O. Sackur.—When manganese oxides are oxidised in the air in presence of excess of fused potassium carbonate, a potassium mangani-manganate, $Mn_5O_{13}.8K_2O$, is formed—

$$5Mn_2O_3 + 10K_2CO_3 + 11O = 2(Mn_5O_{13}.5K_2O) + 10CO_2$$

$$2(Mn_5O_{13}.5K_2O) + 6K_2CO_3 = 2(Mn_5O_{13}.8K_2O) + 6CO_2.$$

In fused sodium carbonate a mangani-manganate of formula $Mn_2O_5.4Na_2O$ results, probably with the intermediate formation of $MnO_2.2Na_2O$. Thus both the valency and the basicity of the manganese oxide differs in the potassium carbonate and sodium carbonate melts. It is noteworthy that these complex molecules are formed at high temperatures.

Zeitschrift für Anorganische Chemie. Vol. lxx., No. 2, 1911.

Basicity of some Heteropoly Acids.—Arthur Rosenheim and Jacob Pinsker.—The authors have succeeded in preparing a well characterised heptabasic soluble salt of 12-molybdenic acid, and also of a molybdenic acid—arsenic acid, and by measuring their conductivity have shown that these salts are true neutral salts, while the tribasic salts behave like acid salts. This result confirms Miolati's theory of heteropoly acids.

Normal Barium Orthosulpharsenate ($Ba_3As_2S_8+6H_2O$).—Emanuel Glatzel.—Normal barium orthosulpharsenate can be prepared by the action of barium sulphhydrate on arsenic pentasulphide, obtained by adding sulphuretted hydrogen to a solution of arsenic acid containing hydrochloric acid, the sulphuretted hydrogen being always present in excess. The formula is $Ba_3As_2S_8+6H_2O$, and the substance forms large pale yellow needles, which are transparent like glass. It is difficultly soluble in water, undergoing decomposition. On warming it gives up its water of crystallisation, and turns first lemon coloured and then light brown, and on being heated in air it gives off white fumes and leaves behind a white residue.

Preparation of Pure Hydrosulphite.—Karl Jellinek.—In this paper the author describes an apparatus which can be used for the preparation of pure 100 per cent hydrosulphite. It was found that the salting out of the aqueous hydrosulphite solution must be performed quickly or else an impure preparation is obtained. In dehydrating the hydrosulphite hydrate in saturated salt solution a 100 per cent preparation can be obtained only by the addition of alkali. The author has obtained fresh confirmation of the molecular formula $Na_2S_2O_4$ by determinations of the conductivity and freezing-point.

Zinc Chromates.—Max Gröger.—When zinc oxide is dissolved in chromic acid solution an acid liquid and a basic residue are obtained. The analysis of the latter shows the presence of the five substances $4ZnO.CrO_3.3H_2O$, $3ZnO.CrO_3.2H_2O$, $4ZnO.2CrO_3.3H_2O$, $3ZnO.2CrO_3.H_2O$, $ZnO.CrO_3.H_2O$.

Hydrazinates of Metallic Salts.—Hartwig Franzen and Hubert L. Lucking.—If aqueous solutions of cobalt iodide or nickel iodide are mixed with an aqueous solution of hydrazine iodide the solution remains clear at first, but after a time a powdery precipitate begins to separate. Analysis shows that it consists of cobalt iodide dihydrazine or the corresponding salt of nickel iodide. The equations are $CoI_2+2N_2H_4HI=CoI_2(N_2H_4)_2+2HI$, $NiI_2+2N_2H_4HI=NiI_2(N_2H_4)_2+2HI$. These two substances are relatively stable towards water. No hydrazinates are obtained when the chlorides or bromides of cobalt or nickel are mixed with the corresponding hydrazine salts, but double salts result, *e.g.*, $CoBr_2(N_2H_4HBr)_2.4H_2O$. Hydrazine cyanide can be prepared by shaking anhydrous hydrocyanic acid with freshly distilled hydrazine hydrate. It forms hydrazinates with $Cd(CN)_2$, $Zn(CN)_2$, AgCN, &c.

Alloys of Silver and Cadmium.—G. J. Petrenko and A. S. Fedorow.—In the liquid state silver and cadmium mix in all proportions. In the crystalline state they form a series of solid solutions. The compound AgCd is formed in the solid state at 200°. Compounds $AgCd_4$ and $AgCd_3$ possibly exist, and Ag_2Cd_3 is a very probable compound.

Reactions of Mercurous Chloride.—W. Herz.—Mercurous chloride reacts with caustic alkali according to the equation $Hg_2Cl_2+2KOH \rightleftarrows Hg_2O+H_2O+2KCl$, and the values $[KOH]:[KCl]$ in three experiments were found to be 0·0152, 0·0166, 0·0166. With sodium carbonate the equation is $Hg_2Cl_2+Na_2CO_3=Hg_2CO_3+2NaCl$, and the values of $[Na_2CO_3]:2[NaCl]$ were 1·65, 1·69, 1·30, 1·38.

INDEX.

ABBOTT, P., Association of Teachers in Technical Institutions, 83
Absorptive power, influence of conjugated linkings on general, 116, 297
Acetate, chromic, basic violet, 131
Acetone, condensation in presence of phosphoric acid, 167
preparation of ketene from, 130
Acetylbenzoin, nitration, 115
Acetyl chloride and salicylamide, condensation, 225
Acid, acetic, detection and estimation of small quantities of acetic anhydride in, 249
ethyl alcohol, ethyl acetate, and water, equilibrium in system, 287
purification, 248
α-aminolauric, dipeptides of, synthesis with glycine, alanine, valine, leucine, and asparagine, 141
aminolauronic, derivatives, 297
chromic, and salts, catalysis by, 96
citric, solutions, determination of zinc from, 15
dithionic, rate of decomposition of dissolved, 204
formic, and cellulose, interaction, 295
malonic, condensation of acrolein bromide with, 95
mannitoboric, 272
metaboric, and metaphosphoric acid, behaviour in melts of their alkali salts, 95
metatungstic, 132
γ-methylbutane-αβδ-tricarboxylic, synthesis, 222
dl-1-methyl-Δ³-cyclohexene-3-carboxylic, resolution of, 141
as-methylethylsuccinic, synthesis, 116
nitric, action on aloins, 36
and copper, interaction in presence of metallic nitrates, 115
nitromyristicinic, orientation of nitro-group in, 78
1-nitroso-2-naphthol-3 : 6-disulphonic, monosodium salt of, 256
orthophosphoric, as a dehydrating agent, 167
second and third dissociation constants of, 249
pentane-αβδ-tricarboxylic, synthesis, 222
pentathionic, in natural waters, 69
pertitanic, salts of with organic bases, 191
β-phenyl-β-methylvaleric, synthesis, 116
Acid, αβ-phenyl pentenic, transformation into its γδ-isomer, 144
phenylpropionic, ketones derived from, 180
phosphoric, resolution of asymmetrical derivatives of, 165
sulphuric, and aromatic disulphides, interaction, 165
and aromatic disulphoxides, interaction, 285
and aromatic orthohydroxysulphides, interaction, 250
and ether, physical properties of mixtures of, 19
determining, 191
telluric, alkalimetric determination, 132
Acids containing three hydrocarbon residues directly attached to an asymmetric carbon atom, optical properties of, 116
depression of hydrolytic activity of by paraffinoid alcohols and acids, 145
flowing from Thomson displacement apparatus for manufacture of gun-cotton, 116
photolysis of complex by ultraviolet rays, 156
α-alkoxyl, action of chlorides of on organo-metallic compounds of zinc, 156
amino, attempts to prepare glycerides of, 20
complex salts of, 95
carboxylic, preparation of secondary amines from, 225
cinnamic, configuration in case of, 103
dibromosuccinic, configuration of stereoisomeric, 296
2 : 3-di-iodo-, and 2 . 3 : 4 : 5-tetraiodobenzenesulphonic, 69
fatty, and cholesterol, 70
rotation of halogen derivatives of, 249
fluoro- and iodo-benzoic, rotation of menthyl esters of isomeric, 249
glucodeconic, 24, 95
glutaric, formation of ββ-disubstituted, 115
heteropoly, basicity of, 312
iodobenzenemonosulphonic, 69
phosphoric, 79
picraminobenzoic, and their salts, 79
sulphinic, intermolecular condensation of aromatic, 285
toluic, ketones derived from, 120
Acidity of paper, 193
Acrolein bromide, condensation with malonic acid, 95
Actinium and ionium, separation from certain residues, 128
Acylguanidines, aromatic, preparation, 95
Adhikáry, B. B., and P. Neogi. (*See* Neogi, P.)
Adlam, G. H. J., and H. B. Baker. (*See* Baker, H. B.)
Adsorption as preliminary to chemical reaction, 259
Ag-Sn-Pb, ternary system, 275
Air, liquid, plant, 84
oxygen in, volumetric determinatioo, 272
Alcohols, acetylenic, preparation of true, 263
catalytic etherification by fatty acids, 299
α-ketonic, synthesis of secondary, 299
of fatty series, rotations of secondary, 17
Aldehyde, α-bromcrotonic, 156
Aldehydes, aromatic condensation with nitromethane, 78
electrolytic reduction, 285
Alizarin in rhubarb, occurrence of, 224
Alkali metals, density, coefficient of dilatation and alteration of volume on fusion of, 156
dispersion in vapours of, 153
temperature of action on water, 263
bicarbonates, dissociation pressures of, 295
Alkaline sulphates, double sulphates formed by lanthanum and cerium sulphates with, 23
Alkylammonium bases, nitrites of, 167, 249
Alkyloxides of metals, action of hydrogen sulphide on, 142
Alleo, E. T., and J. Johnston, accurate determination of sulphur in pyrites and marcasite, 95
H. N., and H. S., model illustrating passage of light wave through quartz, 311
H. S., path of an electron in combined radial magnetic and electric fields, 246.
Allmand, A. J., elements Cu | Cu_2O alkali | H_2 at 0°, 166
and F. G. Donnan. (*See* Donnan, F. G.)
Alloxan and glycine, interaction, 67
relation of triketohydrindene hydrate to, 223
Almond oil, 189
Aloins, action of nitric acid on, 36
Alpern, R., and C. Welzmann, attempts to prepare glycerides of amino acids, 20
Alumlnium, alterability of, 251
and zinc alloys, constitution, 113
anode films, properties of, 153
Aluminium-magnesium alloys electrical properties, 120
hydroxide, precipitation in granular form, 169
Amalgams containing silver and tin, 67
organic, 231, 257, 268, 280
American Society of Mechanical Engineers, 132
Amides, acid, and products of condensation of malonamides and malonic esters, 167
action of cyanguanidine on, 276
Amines and acetylenic ketones, compounds of, 216
aromatic, nitration of mono- and di-acetylated, 24
preparation of secondary, from carboxylic acids, 225
4 (or 5)-β Aminoethylglyoxaline, formation from histidine, 116
new synthesis of, 215
3-β-aminoethylindole, syntheses and formation from tryptophan, 20
syntheais, 78
α-Amino-α-phenylacetamide and derivatives, 79
Aminoquercetin, 308
Ammonia and stannous chloride, compounds, 263
direct action of radium on, 68
estimation of free, by titration, 13
for commercial purposes, 84
metallic compounds of substituted, 286
syntheais by heat, 283
Ammonium, action of sulphur dioxide on, 300
compounds, asymmetric quaternary, 306
salts, hyarolysis, 116
carbonate, estimation by titration, 13
sulphate and its instability, 116
Amygdalase, 17
Anæsthetics, effect on nerve, 29
Analysis, chemical, new method, 265
harmonic, new method, 310
Ancestry, cancerous, 239
Anderson, A., and J. E. Bowen, measurement of contact differences of potential, 311
André, E., compounds of amines with acetylenic ketones, 216
true cyclic acetylenic hydrocarbons, phenylbutine, 204
Andström, V., rusting of iron, 60
Anhydride, acetic, detection of small quantities in acetic acid, 249
Anhydrides, acetic acid, behaviour at high temperatures, 191
Anhydrocotarninephthalide, 260
Aniline and derivatives, action of chlorides of antimony on, 260

Aniline series, organo-metallic body of, 52
solubility in aqueous solutions of its hydrochloride, 261
hydrochloride, conductivity and viscosity of aqueous solutions of at 25°, 261
solubility of aniline in aqueous solutions of, 261
Anilines, chlorination of, 285
Animal products, determining ash in, 252
Anode, glass-frame, for use with silver and nickel cathodes, 14
Antelope, experiments to ascertain if it may act as a reservoir of the virus of sleeping sickness, 57
Antimony compounds, aromatic, 260
in soft solder, determination, 147
chlorides, action on aniline and its derivatives, 260
Apparatus for maintenance of constant pressures, 165
for making delicate tensile tests, 273
for measuring colour-sensations, 178
for moulding and shaping of ship models, 273
for precipitating, filtering, and drying in an inert gas, 223
for rapid electro-analytical determination of metals, 14
for study of flow past plates and models in stream of water, 273
gyroscopic, 310
Lorenz, 273
Physical Society Exhibition of, 9
radio-telegraphic, 179
spark coil, 9
sublimation, 138
Thomson displacement, for manufacture of gun-cotton, composition of acids flowing from, 116
Apricot kernel oil, 189
Arc, electric, reactions in, 36
Archbutt, S. L., and W. Rosenhain. (*See* Rosenhain, W.)
Armstrong, H. E., banquet in honour of, 228, 253
studies of the processes operative in solutions, 97, 109
and E. F. Armstrong, action of stimulants (hormones) in promoting enzymic activity (digestion), 293
studies on enzyme action, 17
and E. Hurton, studies on enzyme action, 17
and D. Crothers, studies of processes operative in solutions, 121
and J. V. Eyre, studies on enzyme action, 17
and E. Wheeler, studies of processes operative in solutions, 133
and F. P. Worley, studies of processes operative in solutions, 145, 168
Arsenic amalgam, preparation, 263
Ash in animal and vegetable products, determining, 252
Association of Teachers in Technical Institutions, 83 250
Aston, F. W., distribution of electric force in the Crookes dark space, 33
Atkins, W. R. G., cryoscopic. ebullioscopic, and association constants of trimethylcarbinol, 20
Traube's molecular volume method applied to binary mixtures of organic substances, 18
Atmosphere over England, vertical temperature distribution in, 245
rare gases of, 242
Atoms, rationality of ratios of magnetic moments of, 137
Atropine and strychnine, separation and determination, 185
Attfield, J., obituary, 144, 155
Auger, V., oxidation of iodine by hydrogen peroxide, 251
and M. Gabillon, new method of determining sulphuric acid and sulphates, 191
Austin, P. C., interaction of silver nitrate and potassium persulphate, and its catalytic effect in the oxidation of organic substances, 80
Autoagglutination of red blood cells in trypanosomiasis, 57
Ayrton, Mrs. Hertha, some new facts connected with the motion of oscillating water, 66
Azo-derivatives of phenylisoxazolone, 228

B. LACTIS aerogenes, action on glusose and mannitol, 57
Bacillus of long life, 304
phosphorescens, photographs and living cultures of, 293
Backe, A., A. Wiborg, and E. Roer, analysis of sweetened condensed milk, 129
Bacteria, variation and adaptation in, 178
Bagster, L. S., properties of binary mixtures of some liquefied gases, 286
Bailey, G. H., and H. W. Bausor, "Chemistry for Matriculation" (review), 190
Bairstu, G. E., and R. Mercer, some properties of aluminium anode films, 153
Baker, G. S., apparatus for moulding and shaping of ship models, 273
H. B., ionisation of gases and chemical change, 173
and G. H. J. Adlam, constancy of water of crystallisation in hydrated salts, 78
Sarah M., theory regarding configuration of certain unsaturated bodies, 102
Balareff, D., products obtained by dissolving phosphorus pentoxide in water, 101
Baly, E. C. C., absorption spectra of chlorobenzene, the dichlorobenzenes, and chlorotoluenes, 167
Bamberger, E., behaviour of acetic acid anhydride at high temperatures, 191
Bangor, "University College of North Wales Calendar" (review), 227
Barbieri, G. A., complex molybdates of rare earths, 168
and F. Calzolari, compounds of salts of rare earths with hexamethylenetetramine, 275
new compounds of hydrated metallic salts with hexamethylenetetramine, 192
and F. Lanzoni, hydrated addition products of metallic bichromates, 275
Bargellini, G., derivatives of oxyhydroquinone, 168
Barium orthosulpharsenate, normal, 312
Barker, T. P., note on a colour change in β-paranitrophenol brought about by sunlight, 306
Barnard, J. E., and R. T. Hewlett, method of disintegrating bacterial and other organic cells, 239
Barnett, E. de B., note on preparation of thiobenzanilide, 68 and H. Leete. (*See* Leete, H.)
Barometer, 9
Barratt, J. O. W., complement deviation in mouse carcinoma, 77
Barre, M., double sulphates formed by sulphates of lanthanum and cerium with alkaline sulphates, 23
Barrett, W. H., and H. Hartley. (*See* Hartley, H.)
Baskerville, C., and L. J. Curtman, "Course in Qualitative Chemical Analysis" (review), 190
Bassett, H., jun., and H. S. Taylor, interaction of metallic oxides and phosphoryl chloride, 297
Bateman, Capt. H. R., Col. Sir D. Bruce, and Capt. A. E. Hamerton. (*See* Bruce, Col. Sir D.)
Batey, J. P., notes on formation of hypoiodites and their action on sodium thiosulphate, 130
Battery, 10,000 volt storage, 130
Bauer, E., and A. Haller. (*See* Haller, A.)
Bausor, H. W., and G. H. Bailey. (*See* Bailey, G. H.)
Baxter, G. P., and H. C. Chapin, revision of atomic weight of neodymium, 186, 195, 209, 218, 229
Bayliss, W. M., properties of colloidal systems, 259
Beadle, C., and H. P. Stevens, "Rubber" (review), 287
Beard, S. H., and J. J. Sudborough. (*See* Sudborough, J. J.)
Beck, R. and J., Beck-Gordon lamp, 9
Thorp diffraction grating, 9
Becquerel, J., duration of phosphosescence of uranyl salts, 216
Beilby, G., Address to Institute of Chemistry, 117.
Bell, Sir W. J., "Sale of Food and Drugs Act" (review), 11
Bellucci, I., direct synthesis of glycerides, 276
and R. Manzetti, direct synthesis of glycerides, 192
and G. Sabatini, structural isomeriam in metallic cyanides, 276
Bennett, C. T., and J. C. Umney. (*See* Umney, J. C.)
Benzene derivatives, absorption spectra of, 116
Benzoyl derivatives, use of metallic potassium in determining halogens in, 1
Benzylammonium series, nitrites of, 261
nitrite and its sublimation and decomposition by heat, 261
Benzyl cyanide, action of ether-salts on monosodium derivatives of, 95
Berberine, constitution, 307
Berger, E., tetranitromethane, 12
Bergman, M., and J. Schmidlin. (*See* Schmidlin, J.)
Berry, A. J., occlusion of hydrogen by palladium-gold alloys, 141
Berthelot, D., and H. Gaudechon, action of ultra-violet rays on linear and cyclic organic compounds, 180
nutrification by ultra-violet rays, 240
photolysis of complex acids by ultra-violet rays, 156
principal types of photolysis of organic compounds by ultra-violet rays, 94
Bertrand, G., and G. Weisweiller, constitution of vicianose and vicianine, 24
Besson, A., and L. Fournier, brominated and hydrobrominated compounds of silicon, 36
reduction of phosphorus oxychloride by hydrogen under action of electric discharge, 23
silicon chlorobromides and chloroiodides, 228
Bevan, E. J., and C. F. Cross. (*See* Cross, C. F.)
P. V., absorption spectra of lithium and cæsium, 152
dispersion in vapours of alkali metals, 153
Bichromates, metallic, hydrated addition products of, 275
Bicknell, H. R., F. C. Frary, and C. A. Tronson. (*See* Frary, F. C.)
Binary mixtures of organic substances, Traube's molecular volume method applied to, 18
systems, 95
Bismuthides, some well-defined, 252
Black, J. W., and T. Cockburn. (*See* Cockburn, T.)
Blackman, F. F., and A. M. Smith, experimental researches on vegetable assimilation and respiration, 92
Blaise, E. E., and L. Picard, action of chlorides of α-alkoxyl acids on mixed organometallic compounds of zinc, 156, 191
formation of ethyl chlorethoxyacetate, 288
Bland, N., W. H. Perkin, jun., and R. Robinson, iso-oxyberberine, 142
Blaud's pills, composition, 240
Bleaching process, action of carbon dioxide in, 166
Blood, action of radium emanations upon some main constituents of normal, 284
Bodroux, F., action of ether-salts on monosodium derivatives of benzyl cyanide, 95
Bolton, E. R., and C. Revis, methods of estimating cocoanut oil and butter in butter and margarine, 274
Boltwood, B. B., report on separation of ionium and actinium from certain residues, and production of helium by ionium, 128
Bomb calorimeter, friction in, 2
Bombax malabaricum, gum from, 179
Bongrand, J. C., and C. Moureu. (*See* Moureu, C.)

Books, Reviews and Notices of—
"Absorption," 130
"Alchemy, Ancient and Modern," 240
"Alcoholic Fermentation," 311
"Alcohols, Hydrocarbons, and Ethers of Fatty Series," 275
"Allen's Commercial Organic Analysis," 311
"Analysis, Chemical, Course in Qualitative," 190
"Analysis, Chemical, Qualitative," 190
"Analysis, Organic, Allen's Commercial," 311
"Analysis, Volumetric, New Reduction Methods in," 93
"Aniline Lakes, Tests for Coal-tar Colours in," 93
"Argon, Measurements Relating to the Equation of Condition for," 144
"Arizona, Mineralogy of," 143
"Aynsome Annual," 23
"Botany and Pharmacognosy, Text-book of," 94
"Cadmium, Zinc, Copper, Mercury," 119
"Cane-sugar," 299
"Carbon Compounds, Electrical Double Refraction of," 94
"Chemical Theory, Introduction to," 250
"Chemists' Pocket Manual," 11
"Chemistry, Agricultural, Course of Practical Work in," 299
"Chemistry, Applied, Dictionary of Technology and of," 94
"Chemistry, Bacteriological and Enzyme, Introduction to," 251
"Chemistry, Class-book of," 287

Books, Reviews and Notices of—
" Chemistry, Colloidal, Outlines of," 251
" Chemistry, Concise History of," 287
" Chemistry, Elementary, for Coal-mining Students," 311
" Chemistry, Experimental, Outlines of," 22
" Chemistry for Matriculation," 190
" Chemistry, General, Introduction to," 118
" Chemistry, Inorganic, for Advanced Students," 143
" Chemistry, Inorganic, Manual of Practical," 34
" Chemistry, Inorganic, New Ideas on," 215
" Chemistry of Coal," 119
" Chemistry, Organic, Introduction to Practical," 118
" Chemistry, Organic, Laboratory Notes on," 59
" Chemistry, Organic, of Nitrogen," 59
" Chemistry, Organic, Textbook of," 23, 227
" Chemistry, Physical, Introduction to," 118
" Chemistry, Physiological, Practical," 23
" Coal, Chemistry of," 119
" Coal Dust, Explosibility of," 240
" Coal-mining Students, Elementary Chemistry for," 311
" Coal-tar Colours in Aniline Lakes, Tests for," 93
" Colloids, Introduction to the Chemistry of," 34
" Colour and Constitution in Organic Compounds, Relation between," 299
" Copper, Zinc, Cadmium, Mercury," 119
" Crystallography and Practical Crystal Measurement," 215
" Denver Fire-clay Company's Catalogue of Assayers' and Chemists' Supplies," 11
" Dictionary of Technology and of Applied Chemistry," 94
" Dictionary, Webster's New International," 93
" Diet and the Maximum Duration of Life," 34
" Dioxydiaminoarsenobenzol or Salvarsan," 190
" Dispensing made Easy," 130
" Drugs Act, Bell's Sale of Food and," 11
" Elements, M.C.C. Chart of the," 119
" Encyclopædia Britannica," 58, 107, 154
" Ethers. Hydrocarbons, and Alcohols of Fatty Series," 275
" Explosibility of Coal Dust," 240
" Explosives, Primer on, for Coal Miners," 143
" Fats, The," 10
" Fermentation, Alcoholic," 311
" Fermentation, Micro-organisms and," 227
" Fire Tests with Textiles," 10
" Food and Drugs Act, Bell's Sale of," 11
" Food-testing, Elementary Course on," 43
" Gas Manufacture, Text-book of, for Students," 250
" Green Book of London Society," 275
" Griffin's Scientific Handicraft," 11, 35
" Hydrocarbons, Alcohols and Ethers of Fatty Series," 275
" Indiarubber and its Examination," 94
" Invisible, Seeing the," 48
" Iron and Steel Analysis," 34
" Iron and Steel Works Analyses, Practical Guide to," 275
" Iron Founding, Lectures on," 287
Books, Reviews and Notices of—
" Language, Science of Poetry and the Philosophy of," 22
" Lewis's Medical and Scientific Circulating Library," 91
" Life, Diet and the Maximum Duration of," 34
" Literature of Medicine and Natural Science," 190
" London Society, Green Book of," 275
" Manchester, Journal of the Municipal School of Technology," 190
" Manuring of Market-garden Crops," 94
" Mass in Chemical Transactions, Conservation of," 94
" Matriculation, Chemistry for," 190
" Matriculation, Directory," 251
" Medicine and Natural Science, Literature of," 190
" Merck's Index," 227
" Mercury, Zinc, Cadmium, Copper," 119
" Metallurgy, Introduction to the Study of," 10
" Micro-organisms and Fermentation," 227
" Mineralogy of Arizona," 143
" Mycology, Technical," 34
" Nitrogen, Organic Chemistry of," 59
" Oils, Ethereal," 23
" Organic Compounds, Relation between Colour and Constitution in," 299
" Philosophy, Chemical, Sketch of a Course of," 34
" Photography in Colours," 11
" Physical Measurements," 216
" Poetry, Science of, and the Philosophy of Language," 22
" Reagents, Standards, and Tests, Analytical," 250
" Rubber," 287
" Salvarsan or '606,'" 190
" Science of Poetry and the Philosophy of Language," 22
" Scientist's Reference Book and Diary," 11
" Seeing the Invisible," 48
" Sewage, Clarification of," 250
" Sewage Purification, Modern Methods of," 311
" Soil Constituent, some Effects of a Harmful Organic," 119
" Technology, Dictionary of, and of Applied Chemistry," 94
" U.S. Department of Agriculture, Report of Chemist for 1910," 311
" University College of North Wales Calendar," 227
" Webster's New International Dictionary," 93
" Who's Who in Science," 300
" Zinc, Cadmium, Copper, Mercury," 119

Booth, E. H., reduction of silver chloride, 288
Borax, D., some reducing actions of mercury, 261
Bossuet, R., and L. Hackspill. (*See* Hackspill, L.)
Bouchonnet, A., " Zinc, Cadmium, Cuivre, Mercure " (review), 119
Bougault, J., transformation of αβ-phenyl pentenic acid into its γδ-isomer, 144
Bousfield, W. R., and W. E. Bousfield, specific heat of water, 128
Bowden, R. C., studies of constitution of soaps in solution, 68
Bowen, J. E., and A. Anderson. (*See* Anderson, A.)
Boxwood, South African, pharmacological action of, 57
Boyle, Mary, iodobenzenesulphonic acids, 69
Brady, O. L., compounds of copper benzoate with pyridine and quinoline, 222
Bragg, W. H., and H. L. Porter, energy transformations of X-rays, 270
Brass foundry, fluxes as applied to, 31
Breteau, P., complete destruction of organic matter for detection of inorganic poisons, 144
hydrogenation in presence of palladium, 72
Brewing, industry of, 129
Briggs, S. H. C., isomerism of ferrocyanides, 80
Brizard, L., and M. de Broglie (*See* de Broglie, M.)
Brodie, T. G., new conception of glomerular activity, 305
Bromide, cupric, dissociation, 116
Bromine, determination in presence of chlorides and iodides, 204
vapour pressure and apparent superheating of solid, 270
Bromobenzene, absorption spectra, 167
ω - Bromomethylfurfuraldehyde, reactions of, 272
6-Bromo-2-phenyldihydro-1 : 3-benzoxazine-4-one and related derivatives, 20
Bromo-salts of platinum, 84
Broniewski, W., electrical properties of aluminium-magnesium alloys, 120
Bronze, hydraulic, 91
Bronzes, tempering of, 23
Brown, J. H., and J. A. N. Friend (*See* Friend, J. A. N.) and T. E. Hull. (*See* Friend, J. A. N.)
M., " Chemistry of Coal " (review), 119
Bruce, Col. Sir D., and Capts. A. E. Hamerton and H. R. Bateman, experiments to ascertain if antelope may act as a reservoir of the virus of sleeping sickness, 57
domestic fowl of Uganda may act as a reservoir of the virus of sleeping sickness, 58
Brühl, J. W., obituary, 84
Bryant, E. G., new ferments, 108
Bryony-root, constituents of, 248
Bunsen centenary, 131
Buphane disticha, constituents of bulb of, 295
Burch, G. J., method of measuring colour-sensations by intermittent light, with description of an unfinished apparatus for the purpose, 178
Bureau of Mines, work of the chemical laboratories of, 49
Burger, O. K. H., sensitiveness of pentamminenitrosocobalt salts to light, 307
Burgess, G. K., and C. W. Waidner. (*See* Waidner, C. W.)
M. J., and R. V. Wheeler, volatile constituents of coal, 166
Burrell, B. A., " An Elementary Course on Food-testing " (review), 48
Burt, F. P., and R. W. Gray, weight of a normal litre of hydrogen chloride, and atomic weight of chlorine, 161, 170
Butcher, Dr. D., examples of osmotic growths, 293
Butter, cocoanut oil in, methods of estimating, 274
Butyl cyclohexane derivatives, 228

$C_{18}H_8S_8$ and derivatives, 120
Cadmium and silver alloys, 312
and tellurium alloys, 60
Cæsium, absorption spectra, 152
Calcium and strontium, separating and identifying, sulphite method, 157
metallic, efficiency in electrolytic production, 7
Calcium carbide, use for determining moisture, 37
Callendar, H. L., action of electric thermo-regulator, 262
Calorimeter bomb, friction in, 2
gas, still-water, 117
Calorimeters, flow, radiation errors in, 21
Calzolari, J., and G. A. Barbieri. (*See* Barbieri, G. A.)
Campbell, Mr., and Mr. Dye, spark trains, 273
Camphane series, studies in, 139
Camphorquinoxe, phenylhydrazone of, 139
Campion, A., " Iron and Steel Analysis " (review), 34
Cancer in mice, 239
Cancerous ancestry, 239
Cannizzaro, S., " Sketch of a Course of Chemical Philosophy " (review), 34
Capsaicin, 111
Capsicum, pungent principle of, and detection, 111
Carbazole series, studies in, 19
Carbinols, asymmetric, 306
Carbohydrate constituents of Para rubber, 140
Carbon, action of water-vapour on, in presence of lime, 263
assimilation, mechanism of, 284
dioxide, action in bleaching process, 166
monoxide and chlorine, interaction, 141
Carbonyl group, influence on optical rotatory power, 68
Cardell, I. S., and F. Thomas, synthesis of ammonia by heat, 285
Carré, P., Contardi's polyphosphoric ethers of mannite, quercite, glucose, and inosite, 204
" Hydrocarbures, Alcools et Ethers de la Série Grasse " (review), 275
Casella, C. F. and Co., barometer, 9
Castings, nickel steel, 169
Catalysis by chromic acid and its salts, 96
etherification and saponification by, 180, 216
in a homogeneous system, 204
mechanism of negative, 248
Catalytic action of copper oxide, 241
Cathode rays and canal rays, chemical action induced by, 222
Cathodes, lime, behaviour of incandescent, 226
Cattle, causation of hepatic cirrhosis in, 305
Caulophyllin, reaction for, 240
Caven, R. M., and H. J. S. Sand, dissociation pressures of the alkali bicarbonates, 295
Cells, bacterial and other organic, disintegrating, 239
Celluloid in a dangerous form, 12
non-inflammable, 293
Cellulose and formic acid, interaction, 295
mercerised, 131
Celtium, 73
Cerium and lanthanum sulphates, double sulphates formed by, with alkaline sulphates, 23
separation by potassium permanganate, 303
Chada, D., and V. Edwards. (*See* Edwards, V.)
Challenger, F., and F. S. Kipping, resolution of asymmetrical derivatives of phosphoric acid, 165
Chambers, Helen, and S. Rust, action of radium radiations upon some of main constituents of normal blood, 284
Chapin, H. C., and G. P. Baxter. (*See* Baxter, G. P.)
Chapman, A. C., industry of brewing, 129
D. L., and F. H. Gee, interaction of chlorine and carbon monoxide, 141

Chattaway, F. D., oxidation and auto-reduction of hydrazines, 217
Chauvenet, E., general method of preparing anhydrous chlorides, 120
Cheese, transformation of proteids into fats during ripening, 57
Chelsea, South-Western Polytechnic Institute, 96
Chemical action induced by cathode rays and canal rays, 222
compounds and living muscle-proteins, reactions between, 67
constitution and hypnotic action, 167
Engineering and Industries Exhibition, 12, 96, 238
Engineering Exhibition, exhibitors' dinner, 269
qualifications, 144
Societies, International Association of, 271
Society, 17, 66, 77, 113, 139, 164, 221, 248, 252, 260, 271, 285, 295, 305
Report of the Council, 212
Chemistry, recent advances and problems in, 123, 136
Chemists' Building, New York City, formal opening, 235
Chick, action of X-rays on developing, 57
Chicken fat, constants for, 189
Chlorides, anhydrous, preparing, 120
of α-alkoxyl acids, action on organometallic compounds of zinc, 156, 191
Chlorination, a method of, 285
Chlorine and carbon monoxide, interaction, 141
atomic weight, 161
Chlorobenzene, absorption spectra, 167
Chlorophyll, crystallised, 51
Chloro-salts of osmium, 84
Chlorotoluenes, absorption spectra, 167
Cholesterol and fatty acids, 70
Chou, T. Q., and W. H. Perkin, jun., experiments on synthesis of terpenes, 142
Chromium, alloys of nickel and cobalt with, 201
Cinchonine and isomerides, absorption spectra, 295
Circuits, oscillatory currents in coupled, 179
Clark, S. G., and F. Ibbotson. (*See* Ibbotson, F.)
Clarke, C H., and F. Francis, α-amino-α-phenylacetamide and derivatives, 79
R W., determination of amount of dissolved oxygen absorbed by sewage effluents containing nitrites, 274
Clausmann, P, determination of bromine in presence of chlorides and iodides, 204
Clement, J K., work of the chemical laboratories of the Bureau of Mines, 49
Clewer, H. W. B., and F. Tutin. (*See* Tutin, F.)
Coal, volatile constituents of, 166
Coates, J., "Seeing the Invisible" (review), 48
Cobalt and nickel, alloys with chromium, 201
ammines, configuration determination among, 102
Cocaine and strychnine, separation and determination, 185
Cockburn, T., and J. W. Black, estimation of quinine as the acid citrate in organic liquids, 274
Cohen, J. B., relation of position isomerism to optical activity, 249
Coker, E. G., and S. P. Thompson. (*See* Thompson, S. P.)
Collodi, F., measurement of charge carried by magnetic rays, 168
Colloidal systems, properties of, 259
Colour, discrimination of, 260
Colour-sensations, measuring by intermittent light, 178
Colourless papers, chemically prepared, 192
Columbium and tantalum, separating, 103
determining, indirect method, 52
Comet, Halley's, photographs and spectrograms of, 294
Comets tails, spectrum photographs showing composition of, 294
Condensation of halogen derivatives with ββ-dimethylglycidic ether, 191
Condensers traversed by high frequency electric oscillations, measurement of energy losses in, 81
Conductivity, electrical, depression by non-electrolytes, 121
Configuration of unsaturated bodies, 102
Constants and numerical data, annual tables of, 264
Constitution, utilisation of magnetic field to determine, 192, 204
Contardi's polyphosphoric ethers of mannite, quercite, glucose, and inosite, 204
Cook, S S., and C. A. Parsons. (*See* Parsons, C A.)
Cooke, W. T., and E. H. Rennie. (*See* Rennie, E. H.)
Cooper, W. F., and W. H. Nuttall, some reactions of ω-bromomethylfurfuraldehyde, 272
Copper alloys, gases occluded in, 24
and nitric acid, interaction in presence of metallic nitrates, 115
cast, of high electrical conductivity, 187
derivative of quinol, 305
acetylide, 191
benzoate, compounds with pyridine and quinoline, 222
oxide, catalytic action of, 241
sulphate, action of sodium hypophosphite on, in aqueous solution, 256
Coppola, A., and E. Oliveri-Mandala. (*See* Oliveri-Mandala, E.)
Cornus paniculatum, fruit of, 172
Corrosion of iron, 138
Cossor and Co., X-ray tube, 9
Coste, J. H., and B. R. James, new still-water gas calorimeter, 117
radiation errors in flow calorimeters, 21
and L. M. Nash, further contribution to the question of turpentine substitutes, 190
and W. E. F. Powney, testing of incandescent mantles, 21
M., metallography of system gold-tellurium, 263
Cotton and nitrated cotton, 297
cakes, abnormal, 190
Coumaranone derivatives, 224
Creosote testing, 227
Cribb, C. H., and P. A. E. Richards, notes on analysis of margarine, 274
Crocker, J. C., and F. Matthews, picram nobenzoic acids and their salts, 79
Crommelin, C. A., "Metingen betreffende de toestandsvergelijking van Argon" (review), 144
Crompton, H., and Maggie Walker, reduction of nitroacenaphthene, 309
Crookes, H., photographs and living cultures of bacillus phosphorescens, 293
Sir W., collection of radiometers and otheoscopes, 234
presentation of portrait of to Royal Society, 92
Crookes dark space, distribution of electric force in, 33
Croonian lecture, 305
Cross, C. F., and E. J. Bevan, interaction of formic acid and cellulose, 295
Crossley, A. W., and C. H. Hampshire, 6-nitro-3 : 4 : 3' : 4'-tetramethyldiphenyl, 214
and Nora Renouf, hydroaromatic ketones, 285
Crothers, D., and H. E. Armstrong. (*See* Armstrong, H. E.)
Crowther, J. A., energy and distribution of scattered Röntgen radiation, 66
Crymble, C R., relation between absorption spectra of metallic ions and their valency, 166
A. W. Stewart, R. Wright, and W. G. Glendinning, influence of conjugated linkings on general absorptive power, 116
and Florence W Rea, influence of conjugated linkings on absorptive power, 297
Crystal structure, chemical significance of, 149, 153, 203
Cumming, A C., efflorescence of washing soda crystals, 48
C. A., and A. Gemmell, estimation of ferrous iron by permanganate in presence of hydrochloric acid, 129
Cupreine, reaction of, 84
Cupritartrates and analogous compounds, 68
Current transformer, 9
Currents, oscillatory, in coupled circuits, 179
phase difference between primary and secondary, of a transformer, 80
Curtman, L. J., and C. Baskerville. (*See* Baskerville, C.)
Curves, resonance, taken with impact and spark ball dischargers, 81
Cushney, A. R, action of senecio alkaloids and causation of hepatic cirrhosis in cattle, 305
Cuthbertson, C., and Mrs. M. Cuthbertson, optical method of measuring vapour pressures, 270
Cyanacetylene, 24
Cyanguanidine, action of nitrites on, 276
on amides, 276
Cyanides, metallic, structural isomerism in, 276
Cyclopentanone, catalytic hydrogenation of, 264

DARZENS, G., condensation of halogen derivatives with ββ-dimethylglycidic ether, 191
new method of preparing glycidic ethers, 24
and H. Rost, butyl cyclohexane derivatives, 228
and J Sejourné, condensation of ββ-dimethylglycidic ether with biomacetic ether, 300
Datta, R. L., and P. C. Ray. (*See* Ray, P. C.)
Davies, H., and F. S. Kipping, different methods of applying the Grignard reagents, 114
S H, "Micro-organisms and Fermentation" (review), 227
De Boisbaudran, L. dehydration of salts, 180
De Broglie, M., and L. Brizard, radiation of quinine sulphate, ionisation and luminescence, 131
De Coninck, Œ., molecular weight of uranous oxide, 312
W. Œ., determination of molecular weight of uranous oxide, 251
De Dzierzbicki, J. and J. de Kowalski. (*See* de Kowalski, J.)
De Forcrand, M., probable chemical properties of radium and its compounds, 120
De Forcrand, M., hydrates of potassium fluoride, 299
De Kowalski, J., progressive phosphorescence at a low temperature, 11
and J. de Dzierzbicki, progressive phosphorescence spectra of organic compounds at low temperatures, 24
De Luc, A., and F. Reverdin. (*See* Reverdin, F.)
De Mosenthal, H. observations on cotton and nitrated cotton, 297
Deerr, N., "Cane-sugar" (review), 299
Delachanal, B, and G. Guillemin. (*See* Guillemin, G.)
Delépine, M., action of pyridine on iridodisulphates, 23
Denigès, G., new reaction of cupreine, 84
of morphine, 36
Dewar, Sir J., radiometer motion stopped by a very high vacuum, 293
Diazomethane, esterification of isoxazolones with, 276
Dibenzylammonium nitrite and its sublimation and decomposition by heat, 261
Dichlorobenzenes, absorption spectra, 167
Diethylenesulphidemethylsulphine hydroxide, decomposition in aqueous solution, 286
Dihydro-β-naphthol sulphide, constitution, 250
dl-3 : 4-dihydroxyphenylalanine, synthesis of, 141
Dimethylammonium nitrite, 167, 249
Dines, W. H, vertical temperature distribution in the atmosphere over England, 245
Dinitrodihydroxybenzenes, salts of, 71
3 : 5-Dinitroquinol, salts of, 223
Dipeptides of α aminolauric acid, synthesis with glycine, alanine, valine, leucine, and asparagine, 141
Diphenylene, 215
Diphenylethylene, new series of leuco-bases and dyes from, 238
Diphenylmethane orthosulphoxide intramolecular rearrangements of, 67
Dissociation, electrolytic, relationship of molecular association to, 114
Disulphides, aromatic, and sulphuric acid, interaction, 165
Disulphoxides, aromatic, and sulphuric acid, interaction, 285
Dittler, E., thermochemistry of silicates, 132
Divers, E., modification of Raschig's theory of the lead chamber process, 205
Dixon, W. E., pharmacological action of Gonioma kamassi (South African boxwood), 57
Dobbie, J. J., J. J. Fox, and A. J. H. Gauge, diphenylene, 215
and A. Lauder, absorption spectra of cinchonine, quinine, and their isomerides, 295
hydroxycodeine, 18
Dobson, Beasie, and W. H. Perkin, jun., identity of xanthaline and papaveraldine, 67
Doebner and von Miller, mechanism of quinaldine synthesis of, 115
Dole, R B., occurrence of sulphates in river-waters, 289
Donnan, F. G., and A. J Allmand, standard electrode with alkaline electrolyte, 166
Donnington, G. C., "Class-book of Chemistry" (review), 287
Douglas, C. G., and J. S. Haldane, cause of absorption of oxygen by the lungs of man, 301
L. M., bacillus of long life, 304
Driot, M., mercuric oxychlorides, 288

Drying, precipitating, and filtering in an inert gas, apparatus for, 223
Dudding, B. P., and C. C. Paterson. (*See* Paterson, C. C.)
Doff, A. W., and A. W. Ewell, "Physical Measurements" (review), 216
Dumesoil, E., preparation of arsenic amalgam, 263
Dunnington, F. P., cleaning discoloured marble, 264
Dunstan, A. E., and T. P. Hilditch. (*See* Hilditch, T. P.)
and A. G. Mussell, application of viscometry to measurement of rate of reaction, 142
Dupont, G., acetylenic pinacone, 144
Dust explosions, lecture experiments to illustrate, 307
striations, formation by an electric spark, 226
Dye and Campbell, Messrs. (*See* Campbell, Mr)
Dyes and leuco-bases from diphenylethylene, new series, 288
Dyer, B., and F. W. E. Shrivell, "Manuring of Market Garden Crops" (review), 94
Dyke, G. B., and J. A. Fleming. (*See* Fleming, J. A.)
Dynamical value of molecular systems which emit spectra of banded type, 189
Dynamics, chemical, of serum reactions, 178

EARTHS, rare, complex molybdates of, 168
double nitrates of, 131
salts of, compounds with hexamethylene tetramine, 275
Eccles, W. H., and H. Morris-Airey, notes on the electrical waves occurring in nature, 153
Eden, C. G., apparatus for study of flow past plates and models in stream of water, 273
Edridge-Green, F. W., discrimination of colour, 260
Edwards, Muriel G., and K. J. P. Orton, detection and estimation of small quantities of acetic anhydride in acetic acid, 249
and H. King. (*See* Orton, K. J. P.)
V., and D. Chads, note on Kjeldahl's process, 138
Eichengrun, A., non-inflammable celluloid, 293
Electrical conductivity, depression by non-electrolytes, 121
discharges in air, photographic action at a pressure below that of atmosphere, 274
waves occurring in nature, 153
Electricity, atmospheric, over the ocean, 66
Electro-chemical industry in Norway, 192, 246
Electrode, standard, with alkaline electrolyte, 166
Electrolytes, electrolysis of non-aqueous, 110
solubility in aqueous solutions, 260
Electron, path in combined radial magnetic and electric fields, 246
Electroscope, tilted gold leaf, 9
Elements Cu | Cu_2O alkali | H_2 at 0°, 166
radio-active, who first suggested that they are elements undergoing decomposition at ordinary temperatures? 169
Emmett, W. G., and H. O Jones, isomeric monothiophosphates, 167
Emulsions of silver chloride and bromide, differentiation of latent images obtained with, 252
Enamel, methods of analysis for, 28
Endotoxins, bacterial, immunisation by means of, 239
Energy transformations of X-rays, 270
England, vertical temperature distribution in atmosphere over, 245
Enzyme action, studies on, 17
Enzymic activity, action of stimulants in promoting, 293
Ephraim, F., experiments to prepare optically active phosphorus compounds, 275
and E. Lasocki, nitrosulphamide and sulphohydrazide, 300
and H. Piotrowski, action of sulphur and compounds containing sulphur on hydrazine, 300
sulphur dioxide on ammonia, 300
Epicamphor, 309
Equilibrium $2CO \rightleftharpoons CO_2 + C$, effect of temperature and pressure on, 260
in system, ethyl alcohol, acetic acid, ethyl acetate, and water, 287
Espil, R. L., new anhydrous selenites, 180
Esters, malonic, products of condensation of, and acid amides, 167
of bromo-substituted fatty acids, interaction with silver nitrate in alcoholic solutions, 20
Ethenoid and ethinoid unsaturation, 222
Ether, acetic, condensation with its higher homologues, 120
and sulphuric acid, physical properties of mixtures of 19
chlorocarbonic, action on sodium ketones, 228
$\beta\beta$-dimethylglycidic, condensation of halogen derivatives with, 191
with bromatic ether, 300
estimation of traces of water in, 286
salts, action on monosodium derivatives of benzyl cyanide, 94
catalytic condensation by metallic oxides, 251
Ethers, benzoic, preparation, 180
glycidic, method of preparing, 24
phenolic, additive compounds with aromatic polynitro-compounds, 68
polyphosphoric, of mannite, quercite, glucose, and inosite, 204
Etherification by catalysis, 180, 216
catalytic, of alcohols by fatty acids, 299
Ethyl acetate, ethyl alcohol, acetic acid, and water, equilibrium in system, 287
alcohol, acetic acid, ethyl acetate and water, equilibrium in system, 287
hydrochloride, heat of hydrolysis, 287
influence of water on boiling-point of, 165
temperature on basic water value of, 224
Ethylammonium nitrite, 167, 249
Ethyl bromacetate, condensation of ethyl crotonate and ethyl methylacrylate with, 222
chlorethoxyacetate, formation, 283
crotonate, condensation with ethyl cyanoacetate and ethyl bromoacetate, 222
cyanoacetate, condensation of ethyl crotonate and ethyl methylacrylate, 222
methylacrylate, condensation with ethyl cyanoacetate and ethyl bromoacetate, 222
Eustice, J., experiments on streamline motion in curved pipes, 113
Evans, J., and G. E Scott-Smith. (*See* Scott-Smith, G. E.)
P. E., and H. O. Jones. (*See* Jones, H. O.)
Ewell, A. W., and A. W. Duff, "Physical Measurements" (review), 216
Ewins, A. J., synthesis of 3-β-aminoethylindole, 78
and P. P. Laidlaw, syntheses of 3-β-aminoethylindole and its formation from tryptopham, 20
and F. L. Pyman, experiments on formation of 4(or 5)-β-aminoethylglyoxaline from histidine, 116
Explosions, dust, lecture experiments to illustrate, 307
Eyre, J. V., and H. E Armstrong. (*See* Armstrong, H. E.)

FARADAY Society, 153, 246, 274
Fats, methods of analysis and tests, 148
Fedorow, A. S., and G. J. Petrenko. (*See* Petrenko, G. J.)
Fedotieff, P. P., physico-chemical aspects of formation of cuprous iodide, 60
Ferment, alcoholic, of yeast-juice, 139
Ferments, 108
alcoholic, influence of nitrates on, 12
Ferrocyanides, isomerism of, 80
Feytis, E., magnetism of complex salts, 251
Fichter, F., and P. Sjöstedt, electrolytic oxidation of aromatic sulphides, 131
Films, aluminium anode, 153
Filtering, precipitating, and drying in an inert gas, apparatus for, 223
Firth, J. B., and J. E. Myers, action of sodium hypophosphite on copper sulphate in aqueous solution, 286
apparatus for precipitating, filtering, and drying in an inert gas, 223
Fischer, E., recent advances and problems in chemistry, 123, 136
Fleming, J. A., note on experimental measurement of high-frequency resistance of wires, 80
and G. B. Dyke, measurements of energy losses in condensers traversed by high frequency electric oscillations, 81
resonance curves taken with impact and spark ball dischargers, 81
Fleurent, E., and L Lévi, exact method of determining ash in animal and vegetable products, 252
Flow past plates and models in stream of water, apparatus for study of, 273
Fluorine, magnetic properties of, 299
Fluorone derivatives, 140
Flux, method of constant rate of change, as a standard for determining magnetisation curves of iron, 262
Fluxes as applied to brass foundry, 31
Fomin, W., and L. Tchougaeff. (*See* Tchougaeff, L.)
Foote, H. W., and R. W. Langley, indirect method for determining columbium and tantalum, 52
note on recent method for separating tantalum and columbium, 103
Force, electric, distribution in Crookes dark space, 33
Forster, M. O., new organic compounds of nitrogen, 229
Forster, M. O., and S. H. Newman, triazo-group, 78, 297
and F. M. van Gelderen, triazo group, 78
and A. Zimmerli, studies in camphane series, 139
Fournier, L., and A. Besson. (*See* Besson, A.)
Fowler, domestic of Uganda, experiments to ascertain if it may act as a reservoir of virus of sleeping sickness, 58
A., spectrum photographs showing composition of tails of comets, 294
and R. J. Strutt, spectroscopic investigations in connection with active modification of nitrogen, 270
spectrum of nitrogen afterglow, 294
G. J., "Introduction to Bacteriological and Enzyme Chemistry" (review), 251
Fox, J. J., J. J Dobbie, and A. J. H. Gauge. (*See* Dobbie, J. J.)
and A. J. H. Gauge, mannito-boric acid, 272
Francis, A. G., and C. A. Keane, nitration of acetylbenzoin and of stilbenediol diacetates, 115
F., and C. H Clarke (*See* Clarke, C. H.)
Franzen, H., and H. L. Lucking, hydrazinates of metallic salts, 312
Frary, F. C., H. R. Bicknell, and C. A. Tronson, efficiency in electrolytic production of metallic calcium, 7
Friend, J. A. N., and J. H. Brown, action of salt solutions and of sea-water on iron at various temperatures, 305
T. E. Hull, and J. H. Brown, action of steam on iron at high temperatures, 250
J. N., corrosion of iron, 138
Fruit of Cornus paniculatum, 172
Viburnum lentago, 205
Fuller, H C., separation and determination of cocaine and strychnine, and atropine and strychnine, 185
Funk, C., synthesis of *dl*-3:4-dihydroxyphenylalanine, 141

GABILLON, M., and V. Auger. (*See* Auger, V.)
Gadolinite earths, new element accompanying lutecium and scandium in, 73
Galliot, M., and A. Guntz. (*See* Guntz, A.)
Gams, A., and A. Pictet. (*See* Pictet, A.)
Gas and vapour detectors, testing inflammable, 298
and vapour detector, automatic inflammable, 298
calorimeter, still-water, 117
making visible the paths of ionising particles through, 245
Gases, charges on ions in, 33
evolved by walls of glass, porcelain, and silica tubes, 257
ionisation of, and chemical change, 173
occluded in copper alloys, 24
physical properties of inactive, 71
properties of binary mixtures of liquefied, 286
rare, of atmosphere, 257
Gaskell, J. F., action of X-rays on developing chick, 57
Gaudechon, H., and D. Berthelot. (*See* Berthelot, D.)
Gauge, A. J. H., J. J. Dobbie, and J. J. Fox. (*See* Dobbie, J. J.)
and J. J. Fox (*See* Fox, J. J.)
Gauthier, D., synthesis of secondary α-ketonic alcohols, 299
Gee, F. H., and D. L. Chapman. (*See* Chapman, D. L.)
Geibel, W., electrical and mechanical properties of alloys of noble metals, 60

Gelatin film of dry plates, 10
relationship between size of particles of silver in, and colour of photographic image, 143
Gels, reactions in, 117
Gelsemine derivatives 305
Gemmell, A , and C A. Cumming. (*See* Cumming, C A.)
Gerber's " Neusal " milk test, 189
Gibbs's phase rule, 70
Gilbard, J. F. H., reaction of caulophyllin, 240
Gillette, C. E., fruit of Viburnum lentago, 205
Glass tubes, gases evolved by walls of, 257
Glatzel, E., normal barium ortho sulphareenate, 312
Glendinning, W. G , C. R. Crymble, A. W Stewart, and R. Wright. (*See* Crymble, C. R.)
Glomerular activity, new conception of, 305
β-Glucases in plants, distribution, 17
d-Glucosamine derivatives, 79
Glucose, action of B. lactis aerogenes on, 57
polyphosphoric ethers of, 204
Glycerides of amino-acids, attempts to prepare, 20
synthesis, 192, 276
Glycerin, analysis of crude, 220, 233
Glycine and alloxan, interaction, 67
Gynoscopine, synthesis and resolution of, 224
Godchot, M., hexahydroacetophenone and hexahydrobenzoylacetone, 36
and F. Tarboury, catalytic hydrogenation of cyclo-pentanone, 264
Goerges, H., and O. Ruff. (*See* Ruff, O.)
Goissedet, P., and A. Job. (*See* Job, A.)
Gold, brown, 95, 131
Gold-palladium alloys, occlusion of hydrogen by, 141
tellurium, metallography of the system, 263
Golding, J., note on abnormal cotton cakes, 190
Gerber's " Neusal " milk test, 189
Gonioma Kamassi, pharmacological action of, 57
Goodey, T., contribution to our knowledge of the protozoa of the soil, 284
Goodwin, J. H., determination of tin and 'antimony in soft solder, 147
Gratings, diffraction, 9
Gray, J. A., secondary rays produced by β-rays, 128
R. W , and F. P. Burt (*See* Burt, F. P.)
and Sir W. Ramsay, density of niton (radium emanation) and disintegration theory, 85, 99
Green, Leila, and Brenda Sutherland, decomposition of diethylsulphidemethylsulphine hydroxide in aqueous solution, 286
Greenhill, Sir G., spinning tops and gyroscopic apparatus, 310
and Col. R. L. Hippisley, diagrams of stream lines past an elliptic cylinder, 261
Granet, L., tempering of bronzes, 23
Greth, J. C. W., time, temperature, and composition as factors in softening water, 62
Griffin and Sons, mercurial pump, 9
Grignard, M., two new methods of synthesising nitriles, 191
V., and C Courtot, new derivatives of indone, 156
reagents, different methods of applying, 114
Gröger, M , zinc chromates, 312
Grossman, J , and F. Jones. (*See* Jones, F.)
Guaiacum reaction given by plant extracts, 259
Guichard, M., gases evolved by the walls of glass, porcelain, and silica tubes, 257
Guild, F. N., " Mineralogy of Arizona " (review), 143
Guillemin, G., and B. Delachanal, gases occluded in copper alloys, 24
Gum from Bombax malabaricum, 179
Gun-cotton manufacture, composition of acids flowing from Thomson displacement apparatus for, 116
Guntz, A., and M. Galliot, preparation of crystallised strontium, 12
and J. Minguin, effects of ultra-violet rays, 180
Gussmann, E., basic violet chromic acetate, 131
Gutbier, A., bromo-salts of platinum, 84
chloro-salts of osmium, 84
Gyroscopic apparatus, 310

HAAS, P., " Laboratory Notes on Organic Chemistry " (review), 59
Haber, F., ammonia for commercial purposes, 84
Hackford, J. E., and F. S. Kipping. (*See* Kipping, F. S.)
Hackspill, L., density, coefficient of dilatation and alteration of volume on fusion of alkali metals, 156
and R. Bossuet, temperature of action of alkali metals on water, 263
Haldane, J. S., and C. G. Douglas. (*See* Douglas, C. G.)
Hall, C., and C. E. Munroe. (*See* Munroe, C. E.)
Haller, A., and E. Bauer, action of chlorocarbonic ether on sodium ketones, 228
Halley's comet, photographs and spectrograms of, 294
Halogen-containing compounds, molecular complexity of, 114
derivatives, condensation with ββ-dimethylglycidic ether, 191
of fatty acids, rotation of, 249
Halogens in organic compounds, reactivity of, 20, 248
Hamerton, Capt. A E., Col. Sir David Bruce, and Capt. H. R, Bateman. (*See* Bruce, Col. Sir D)
Hampshire, C. H., and A. W. Crossley. (*See* Crossley, A. W.)
Hanriot, M., brown gold, 95, 131
Harbord, F. W., " Introduction to the Study of Metallurgy " (review), 10
Harden, A., " Alcoholic Fermentation " (review), 311
and S. G Paine, influence of salts on the autofermentation of yeast, 225
and Sir H. Roscoe. (*See* Roscoe, Sir H.)
and W. J. Young, alcoholic ferment of yeast-juice, 139
Harding, V. J., Gertrude M. Walsh, and C. Weizmann, β-methyl-$\Delta^{\alpha\lambda}$-dodecadiene and β-methyl-$\Delta^{\alpha\gamma}$-decadiene, 70
Hartley, H., and W. H. Barrett, determination of density of liquids, 224
W. N., and O. H. Little, course of chemical change in quinol under influence of radiant energy, 285
Hatschek, E., study of reactions in gels, 117
Haworth, H. F., sensitive thermoregulator, 178
W. N., W. H Perkin, jun., and O. Wallach, *dl*- and *d*-$\Delta^{1,8}$-*m*-menthenol(8) and *dl*- and *d*-$\Delta^{1,8}$:8:(9)-*m* menthadiene, 67
Haynes, E., alloys of nickel and cobalt with chromium, 201
Hedley, E. P., " New Ideas in Inorganic Chemistry " (review), 215
Helium, production by ionium, 128
Hepatic cirrhosis in cattle, causation, 305
Hérbet, A., decomposition of metallic xanthates by heat, 263
Herz, W , reactions of mercurous chloride, 312
Herzenstein, Anna, and W. Schlenk. (*See* Schlenk, W.)
Hewlett, R. T , immunisation by means of bacterial endotoxins, 239
and J. E. Barnard. (*See* Barnard, J. E.)
Hexahydroacetophenone, 36
Hexahydrobenzoylacetone, 36
Hexamethylene tetramine, compounds of hydrated metallic salts with, 192
salts of rare earths with, 275
Heycock, C. T., measurement of high temperatures, 179
Hibbert, Eva, and E. Knecht. (*See* Knecht, E.)
Hicks, W. L., and A. W. Titherley. (*See* Titherley, A. W.)
Higgins, S. H., action of carbon dioxide in the bleaching process, 166
W. F., and S. W. J. Smith. (*See* Smith, S. W. J.)
Hilditch, T. P., " Concise History of Chemistry " (review), 287
effect of contiguous unsaturated groups on optical activity, 68
intermolecular condensation of aromatic sulphinic acids, 285
relative effects of ethylenic and acetylenic linkings on optical rotatory power, 68
and A. E. Dunstan, correlation of viscosity with other constitutive properties, 19
viscosity with other physical properties, 222
and S. Smiles, constitution of dihydro-β-naphthol sulphide and interaction of sulphuric acid and aromatic *o*-hydroxysulphoxides, 250
intramolecular re-arrangements of diphenylmethane *o*-sulphoxide, 67
synthesis of derivatives of phenothioxin, 115
Hilger, A , and Co., anomalous dispersion of sodium vapour, 9
Hinda, J. I D., " Qualitative Chemical Analysis " (review), 190
sulphite method for separating and identifying strontium and calcium, 157
Hinrichsen, Dr. F W., and K Memmler, " Der Kautschuk und seine Prüfung " (review), 94
Hippisley, Col. R. L., and Sir G. Greenhill. (*See* Greenhill, Sir G.)
Histidine, formation of 4(or 5) β-aminoethylglioxaline from, 116
r-Histidine, synthesis, 215
Hodges, E. R., organo-metallic body of aniline series, 52
Hodgson, H. H., "Introduction to the Chemistry of Colloids " 34
Hoehn, K., and R. F. Weinland. (*See* Weinland, R. F.)
Holleman, A. F., " Text-book of Organic Chemistry" (review), 227
Holt, A., and J. E. Myers, phosphoric acids, 79
Hope, E., and W. H. Perkin, jun., condensation of ethyl crotonate and ethyl methylacrylate with ethyl cyanoacetate and bromoacetate, 222
and R. Robinson, synthetical experiments in the group of the isoquinoline alkaloids, 260
Hopwood, A., and C. Weizmann, synthesis of dipeptides of α-aminolauric acid with glycine, alanine, valine, leucine, and asparagine, 141
Hornby, J., " Text-book of Gas Manufacture for Students " (review), 250
Hortan, E., H. E. Armstrong, and E. F. Armstrong. (*See* Armstrong, H. E.)
F., vacuum tube spectra of mercury, 271
Houstoun, R. A., absolute measurement of light, 246
Howard, D., efflorescence of washing soda crystals, 48
H., and F. G. Pope. (*See* Pope, F. G.)
Howe, G. W. O , oscillatory currents in coupled circuits 179
radio-telegraphic apparatus, 179
Hughes, E. C., and A. W. Titherley. (*See* Titherley, A. W.)
reaction of potassium iodide on paper, 193
Hull, T. E., J. A. N. Friend, and J. H. Brown. (*See* Friend, J. A. N.)
Humfrey, J. C. W., and W. Rosenhain. (*See* Rosenhain, W.)
Hurtley, W. H., and W. O. Wootton, interaction of alloxan and glycine, 67
Huxley, J. S., some phenomena of regeneration in aycon, with a note on structure of its collar-cells, 239
Hydrazinates of metallic salts, 312
Hydrazine, action of sulphur and compounds containing sulphur on, 300
Hydrazines, oxidation and autoreduction, 217
Hydrindantin and its analogues, 308
β-Hydrindone preparation, 261
Hydrocarbon, aromatic, a new, 215
Hydrocarbons, acetylenic, true cyclic, 204
Hydrogen, occlusion by palladium-gold alloys, 141
reduction of phosphorus oxychloride by, under action of electric discharge, 23
chloride, weight of a normal litre of, 161, 170
cyanide, -detection of traces, 240
dioxide, action on thiobenzanilide, 248
peroxide, decomposition by light, 36
oxidation of iodine by, 251
sulphide, action on alkyloxides of metals, 142
Hydrogenation in presence of palladium, 72
Hydrolytic activity of acids, depression by paraffinoid alcohols and acids, 145
Hydrosulphite, preparation of pure, 312
Hydroxycodeine, 18
Hynd, A., and J. C. Irvine. (*See* Irvine, J. C.)
D. McNicoll, and J. C. Irvine. (*See* Irvine, J. C.)
Hypnotic action and chemical constitution, 167
Hypoiodites, formation and action on sodium thiosulphate, 130

IBBOTSON, F., and S. G. Clark, volumetric determination of uranium, 146
Imino-compounds, formation and reactions, 115
Imperial College of Science and Technology, 193
Indene derivatives, 156
Induction coil, 82
coils, mercury interrupter for, 9
Inglis, J. K. H., optical properties of acids containing three hydrocarbon residues directly attached to an asymmetric carbon atom. 116
Inosite, polyphosphoric ethers of, 204
Institute of Chemistry, Annual General Meeting, 117
Pass List, 59, 216
International Association of Chemical Societies, 271
Iodide, cuprous, formation, physico-chemical aspect of, 60
Iodine in organic compounds, estimation and separation from other halogens, 61
oxidation by hydrogen peroxide, 251
Ionic solubility product, 153
Ionisation, variation with velocity for β-particles, 164
Ionising particles, making visible the paths of, through a gas, 245
Ionium and actinium, separation from certain residues, 128
production of helium by, 128
Ions in gases, charges on, 33
metallic, relation between absorption spectra and valency of, 166
Iridodisulphates, action of pyridine on, 23
Iron, action of salt solutions and sea-water on, at various temperatures, 305
steam on, at high temperatures, 250
and Steel Institute, 158
corrosion of, 138
ferrous, estimation by permanganate in presence of hydrochloric acid, 129
magnetisation curves of, standard for determining, 262
rusting of, 60
Irvine, J. C., and A. Hynd, orthocarboxyanilides of the sugars, 69
D. McNicoll, and A. Hynd, new derivatives of *d*-glucosamine, 79
Isomers, conversion of stable, into labile form by ultra-violet light, 264
Isomerism, position, relation to optical activity, 249
Isomorphism of potassium and sodium compounds, 60
Isooxyberberine, 142
Isoquinoline alkaloids, synthetical experiments in group of, 260
Isospartein, a case of nitrogen stereo-isomerism, 211
preparation of, 191
Isoxazolones, esterification with diazomethane, 276

JACKSON, C. G., dissociation of cupric bromide and some forms of glass manometer, 116
James, B. R., and J. H. Coste. (*See* Coste, J. H.)
C., and L. A. Pratt, basic nitrate of yttrium, 42
Jantsch, G., and S. Wigdorow, double nitrates of rare earths, 131
Jellinek, K., preparation of pure hydroaulphite, 312
Job, A., and P. Goissedet, green crystallised manganitartrate, 156
Johnson, G. L., "Photography in Colours" (review), 11
Johnston, J., and E. T. Allen. (*See* Allen, E. T.)
Jones, C., relationship between size of silver particles in gelatin film and colour of photographic image, 143
F., and J. Grossmann, Bunsen centenary, 131
H. C., bearing of solvate theory of solution, 125
and W. W. Strong, selective oxidation, 188
H. O., and W. G. Emmett. (*See* Emmett, W. G.
and P. E. Evans, mechanism of Doebner and von Miller's quinaldine synthesis, 115
W. J., determination of solubility coefficients by aspiration, 79
W. J., and A. Lapworth, equilibrium in system, ethyl alcohol, acetic acid, ethyl acetate and water, and its displacement by hydrogen chloride, 287
heat of hydrolysis of ethyl alcohol hydrochloride, 287
influence of temparature on basic water value of ethyl alcohol, 224
Jörgensen, A., "Micro-organisms and Fermentation" (review), 227
Joyner, R. A., amalgams containing silver and tin, 67

KAUFFMANN, H., and W. Kugel, 4-nitroresorcin, 312
Kaye, Dr., and J. E. Sears. (*See* Sears, J. E.)
Kayser, E., influence of nitrates on alcoholic ferments, 12
Keane, C. A., and A. G. Francis. (*See* Francis, A. G.)
Kallas, A. M., "Introduction to Practical Organic Chemistry" (review), 118
"Manual of Practical Inorganic Chemistry" (review), 34
Kemmerer, G., electrolytic determination of zinc in ores, 174
Kendall, J., ionic solubility product, 153
Kenner, James, and Emily G. Turner, synthesis of phenanthrene, 221
Kenyon, J., and R. H. Pickard. (*See* Pickard, R. H.)
Kern, S., hydraulic bronze, 91
nickel steel castings, 169
Karr, C. P., determination of lead in non-ferrous alloys, 44
Kershaw, G. B., "Modern Methods of Sewage Purification" (review), 311
Ketene, preparation from acetone, 130
Ketones, acetylenic, and amines, compounds, 216
derived from phenylpropionic acid, 120
toluic acids, 120
hydroaromatic, 285
Kimberley, A. E., "Clarification of Sewage" (review), 250
King, H., and K. J. P. Orton. (*See* Orton, K. J. P.)
and Muriel G. Edwards. (*See* Orton, K. J. P.)
Kipping, F. S., derivatives of silicoethane and silicoethylene, 287
and P. Challenger. (*See* Challenger, F.)
and H. Davies. (*See* Davies, H.) and J. E. Hackford, organic derivatives of silicon, 69
Kjeldahl's process, 138
Knecht, E., and Eva Hibbert, determination of quinone by means of titanium chloride, 131
"New Reduction Methods in Volumetric Analysis" (review), 93
Kobayashi, M., alloys of tellurium with cadmium and tin, 60
Koch, F., and A. Wohl. (*See* Wohl, A.)
Kohn, F., and A. Rosenheim. (*See* Rosenheim, A.)
Kraemer, H., "Text-book of Botany and Pharmacognosy" (review), 94
Kugel, W., and H. Kauffmann. (*See* Kauffmann, H.)
Kuntzen, H., and R. Meldola. (*See* Meldola, R.)
Kurowski, E., and L. Nissenmann, salts of pertitanic acid with organic bases, 191

LACROIX, A., radio-active minerals of Madagascar, 228
Lafar, F., "Technical Mycology" (review), 34
Laidlaw, P. P., and A. J. Ewins. (*See* Ewins, A. J.)
Lamp, Beck-Gordon, 9
Lander, G. D., and A. E. Walden, detection of traces of hydrogen cyanide, 240
Landolt, H., "Über die Erhaltung der Masse bei Chemischen Umsetzungen" (review), 94
Landrum, R. D., methods of analysis for enamel, 28
Lanfry, M., new thiophenic compound, $C_{10}H_8S_2$, and its derivatives, 120
Lang, W. R., note on some metallic compounds of substituted ammonia, 286
and H. Lloyd, lecture experiments to illustrate dust explosions, 307
Langford, T. H., and J. T. Morris. (*See* Morris, J. T.)
Langley, R. W., and H. W. Foote. (*See* Foote, H. W.)
Lankshear, F. R., and W. H. Perkin, jun., epicamphor, 309
Lanthanum and cerium sulphates, double sulphates formed by with alkaline sulphates, 23
Lanzoni, F., and G. A. Barbieri. (*See* Barbieri, G. A.)
Lapworth, A., and W. J. Jones. (*See* Jones, W. J.)
Lasocki, E., and F. Ephraim. (*See* Ephraim, F.)
Lauder, A., and J. J. Dobbie. (*See* Dobbie, J. J.)
Law, H. D., electrolytic reduction, 285
Le Bas, G., relation between molecular volumes and valency numbers, 263
Le Chatelier, H., alterability of aluminium, 251
Le Sueur, H. R., preparation of secondary amines from carboxylic acids, 225
Lead chamber process, chemistry of, 81, 205
in non-ferrous alloys, determination, 44
smelting of materials containing, 275
fluoride, double salts of, and other halogen salts of lead, 275, 276
Leather, J. P., and R. Ross. (*See* Ross, R.)
Leathes, J. B., "The Fats" (review), 10
Lebeau, P., formula of uranium carbide, 288
uranyl nitrate and its ethereal solution, 191
Leete, H., and E. de B. Barnett, note on action of hydrogen dioxide on thiobenzanilide, 248
Legér, E., action of nitric acid on aloins, 36
Leimbach, R., "Die Aetherischen Oele" (review), 23
Leiser, R., "Elektrische Doppelbrechung der Kohlenstoff Verbindungen" (review), 94
Lemoult, P., new series of leucobases and dyes from diphenylethylene, 288
Length, measurement of end-standards of, 34
Leapieau, M., condensation of acroleïn bromide with malonic acid, 95
preparation of true acetylenic alcohols, 263
Leuco-bases and dyes from diphenylethylene, new series of, 288
Lévi, L., and E. Fleurent. (*See* Fleurent, E.)
Lewis, E. A., chemical qualifications, 144
W. C. McC., internal, molecular or intrinsic pressure, 247
Ley, H., "Di Beziehungen zwischen Farbe und Konstitution bei Organischen Verbindungen" (review), 299
Lickfett, H., and O. Ruff. (*See* Ruff, O.)
Life, bacillus of long, 304
Light, absolute measurement of, 246
chemical constitution and absorption of, 46, 55, 64, 75, 90
polarised, experiments with, 293
wave, model illustrating passage through quartz, 311
Linase, 17
Linkings, influence of conjugated on general absorptive power, 116, 297
Liquids, compression at high pressures, 270
determination of density of, 224
Liquorice powder, analytical and microscopical examination of compound, 189
Lithium, absorption spectra, 152
imide, 300
Little, O. H., and W. N. Hartley. (*See* Hartley, W. N.)
Lloyd, C. F., "Bell's Sale of Food and Drugs Act" (review), 11
H., and W. R. Lang. (*See* Lang, W. R.)
London, City and Guilds of, Institute, 171
University, 252
Loram, H. Y., simple method of decomposing refractory tin ores, 143
Lorenz apparatus, 273
Loring, F. H., physical properties of inactive gases, 71
Lowell, P., Lowell Observatory photographs of planets, 175
Observatory, photographs and spectrograms of Halley's comet, 294
Lucking, H. L., and H. Franzen. (*See* Franzen, H.)
Lüders' lines on mild steel, 309
Ludlam, E. B., and H. Preston, "Outlines of Experimental Chemistry" (review), 22
Luff, B. D. W., and W. H. Perkin, jun., experiments on the synthesis of the terpenes, 141
Lumière, L., and A. Seyewetz, differentiation of the latent images obtained with emulsions of silver chloride and bromide, 252
Lungs of man, causes of absorption of oxygen by, 301

McCOY, H. N., and W. C. Moore, organic amalgams, 231, 257, 268, 280
MacDonald, G. W., composition of acids flowing from Thomson displacement apparatus for manufacture of gun-cotton, 116
MacFarlane, W., "Practical Guide to Iron and Steel Works Analyses" (review), 275
McKendrick, Capt. A. G., chemical dynamics of serum reactions, 178
McKenzie, A., configuration of stereoisomeric dibromosuccinic acids, 296

Maclaurin, J. S., occurrence of pentathionic acid in natural waters, 69
McNicoll, D., J. C. Irvine, and A. Hynd. (*See* Irvine, J. C.)
Madagascar, radio-active minerals of, 228
Magini, R., measurement of surface tension, 155
Magnesium aluminium alloys, electrical properties, 120
chloride, action of potassium carbonate on, 228
Magnetic field, utilisation to determine constitution, 192, 204
rays, measurement of charge carried by, 168
storms, origin, 65
Magnetisation curves of iron, standard for determining, 262
Magnetism of complex salts, 251
Magneton, new universal constituent of matter, 137
Mailhe, A., and P. Sabatier. (*See* Sabatier, P.)
Malfitano, G., and A. N. Moschkoff, purification of starch, 12
Malonamides, products of condensation of, and acid amides, 167
Manganates, thermic formation, 312
Manganitartrate, green crystallised, 156
Mannite, polyphosphoric ethers of, 204
Mannitol, action of B. lactis aerogenes on, 57
Manometer, glass, forms of, 116
Mantles, incandescent, testing, 21
Manzetti, R., and I. Bellucci. (*See* Bellucci, I.)
Marble, cleaning discoloured, 264
Marcasite, sulphur in, determination, 95
Marckwald, W., mesothorium, 13
and A. S. Russell, amount of radium contained in some uranium ores, 277
Margarine, analysis, 274
cocoanut oil and butter in, methods of estimating, 274
Marsh, S., and W. H. Nottage, formation of dust striations by an electric spark, 226
Martin, G., who first suggested that the radio-active elements are undergoing decomposition at ordinary temperatures? 169
Martindale, W. H., and W. W. Westcott, "Salvarsan or '606'" (review), 190
Maryott, C. H., use of metallic potassium in determining halogens in benzoyl derivatives, 1
Mason, W., Lüders' lines on mild steel, 309
W. P., contributions to chemistry of sanitation, 278
Masson, I., use of calcium carbide for determining moisture, 37
J. I. O., solubility of electrolytes in aqueous solutions, 260
Mathewson, W. E., and A. F. Seeker. (*See* Seeker, A. F.)
Matter, new universal constituent of, 137
Matthews, F., and J. C. Crocker. (*See* Crocker, J. C.)
Maudsley, F., R. Ross, and J. Race (*See* Ross, R.)
Maxim, H., "Science of Poetry and the Philosophy of Language" (review), 22
May, P., aromatic antimony compounds, 260
note on monosodium salt of 1-nitroso-2-naphthol-3 : 6-disulphonic acid, 286
Mayer, C., "Tests for Coal-tar Colours in Aniline Lakes" (review), 93
Meade, R. K., "Chemists' Pocket Manual" (review), 11
Mees, C. E. K., infra-red photographs, 135
Meldola, R., question of isomerism between naphthiminazoles, 223
and H. Kuntzen, syntheses with phenol derivatives containing a mobile nitro-group, 19, 306
Memmler, K., and F. W. Hinrichsen. (*See* Hinrichsen, F. W.)
Menthyl esters of isomeric fluro- and iodo-benzoic acids, and halogen derivatives of fatty acids, rotation of, 249
Mercer, R., and G. E. Bairsto. (*See* Bairsto, G. E.)
Mercurous chloride, reactions of, 312
Mercury and certain solutions, surface effects between, 154
interrupter for induction coils, 9
reducing actions of, 261
solution in nitric acid, influence of minute quantities of ferric salts and of manganese nitrate on rate of, 67
vacuum tube spectra of, 271
sodium alloys, physico-chemical study of, 181, 198, 207
Merriman, R. W., coumaranone derivatives, 224
and J. Wade. (*See* Wade, J.)
Merton, T. R., absorption spectra of permanganates in certain solvents, 165
Mesothorium, 13
chemistry of, 17
Metals, action of hydrogen sulphide on alkyloxides of, 142
apparatus for rapid electro-analytical determination of, 14
electrical and mechanical properties of alloys of noble, 60
Metallic Compositions Co., "M.C.C. Chart of the Elements" (review), 119
compound of substituted ammonia, 286
Metallography of system gold-tellurium, 263
Δ^2 : 8 : (9)-Meta-menthadiene, 67
dl- and *d*-Δ^2-Meta-menthenol(8), 67
Meteorites, chemistry of, 60
Methylammonium nitrite, 79
β-Methyl-$\Delta\alpha$ 8-dodecadiene and β-methyl-$\Delta\alpha\gamma$-decadiene, 70
Metre bar, silica standard, 273
Meyer, A., azoderivatives of phenylisoxazolone, 228
Mice, cancer in, 239
Milk, analysis of sweetened condensed, 129
composition, 274
test, Gerber's "Neusal," 189
Miller, L., current transformer, 9
O., mercerised cellulose, 131
Minerals, radio-active, of Madagascar, 228
Minguin, J., and A. Guntz. (*See* Guntz, A.)
Moisture, use of calcium carbide for determining, 37
Molecular association and its relationship to electrolytic dissociation, 114
systems which emit spectra of the banded type, dynamical value of, 189
volumes and valency numbers, relation between, 263
Molecules, determination of size of, 312
Molybdates of rare earths, complex, 168
Monosodium derivatives of benzyl cyanide, action of ether-salts on, 94
salt of 1-nitroso-2-naphthol-3 : 6-disulphonic acid, 286
Monothiophosphates, isomeric, 167
Moore, C. W., constitution of scopoletin, 245
α-*p*-hydroxy-*m*-methyoxyphenylethylamine and resolution of α-*p*-hydroxyphenylethylamine, 115
some derivatives of gelsemine, 305
Moore, C. W., and F. B. Power. (*See* Power, F. B.)
R. B., rare gases of atmosphere, 242
W. C., and H. N. McCoy. (*See* McCoy, H. N.)
Morphine, new reaction of, 36
Morris-Airey, H., and W. H. Eccles. (*See* Eccles, W. H.)
Morris, J. T., and T. H. Langford, method of constant rate of change of flux as a standard for determining magnetisation curves of iron, 262
Moschkoff, A. N., and G. Malfitano. (*See* Malfitano, G.)
Mott, O. E., and A. J. Walker. (*See* Walker, A. J.)
Moureu, C., and A. Valeur, isospartein, a case of nitrogen stereo-isomerism, 211
preparation of isospartein, 191
Mouse carcinoma, complement deviation in, 77
Müller, H., occurrence of alizarin in rhubarb, 224
J. A., catalysis in a homogeneous system, 204
rate of decomposition of dissolved dithionic acid, 204
Munroe, C. E., and C. Hall, "Primer on Explosives for Coal Miners" (review), 143
Murray, J. A., cancerous ancestry and incidence of cancer in mice, 239
Muscle-proteins, reactions between chemical compounds and living, 67
Mussell, A. G., and A. E. Dunstan. (*See* Dunstan, A. E.)
Myers, J. E., and J. B. Firth. (*See* Firth, J. B.)
and A. Holt. (*See* Holt, A.)

NANTY, M., action of potassium carbonate on magnesium chloride, and on solutions of magnesium salts in general, 228
Naphthiminazoles, isomerism between, 223
α- and β-Naphthylamine, preparation of heptadecyl and pentadecyl derivatives of, 225
dl-Narcotine, synthesis and resolution of, 224
Nash, L. M., and J. H. Coste. (*See* Coste, J. H.)
National Physical Laboratory, visit of Physical Society, 273
Nelson, E. K., capsaicin, the pungent principle of capsicum, and detection of capsicum, 111
Neodymium, atomic weight, 186, 195, 209, 218, 229
chloride, analysis, 186, 195, 209, 218, 229
Neogi, P., orthophosphoric acid as a dehydrating catalytic agent, 167
trialkylammonium nitrites and nitrites of bases of pyridine and quinoline series, 167
and B. B. Adhicary, preparation of phenylnitromethane, 132
reactions in presence of nickel, 108
Nerve, effect of anæsthetics on, 92
"Neusal" milk test, Gerber's, 189
New York City, Chemists' Building, formal opening, 235
Newman, S. H., and M. O. Forster. (*See* Forster, M. O.)
Newton and Co., mercury interrupter for induction coils, 9
Nickel and cobalt, alloys with chromium, 201
reactions in presence of, 108
steel castings, 169
Nierenstein, M., transformation of proteids into fats during ripening of cheese, 57
Nissenmann, L., and E. Kurowski. (*See* Kurowski, E.)
Niton, density of, 85, 99
Nitrates, influence on alcoholic ferments, 12
of rare earths, double, 131
Nitrated cotton, 297
Nitrification by ultra-violet rays 240
Nitriles, action on cyanguanidine 276
synthesising, 191
Nitrite, cobaltous, change into cobaltic, 104
in sewage effluents or water, determination of amount, 274
Nitrites of alkylammonium bases, 167, 249
of bases of pyridine and quinoline series, 167
of benzylammonium series, 261
Nitroacenaphthene, reduction of, 309
Nitrogen afterglow, spectrum of, 294
chemically-active modification of, produced by electric discharge, 189, 221
organic compounds of, 229
spectroscopic investigation in connection with active modification of, 270
stereo-isomerism, 211
Nitromethane, condensation of aromatic aldehydes with, 78
4-Nitroresorcin, 312
Nitrosates and sodium azide, interaction, 78
Nitrosoazides of pinene and terpineol, 78
Nitrosulphamide, 300
6-Nitro-3 : 4 : 3' : 4'-tetramethyldiphenyl, 214
Niven, C., measurement of specific inductive capacity, 128
Norway, electrochemical industry in, 192
application of hydro-electric plants to, 246
Nottage, W. H., and S. Marsh. (*See* Marsh, S.)
Noyes, W. A., "Text-book of Organic Chemistry" (review), 23
Nuclei, aromatic and hydro-aromatic, relative influences on optical rotatory power, 68
Nuttall, W. H., and W. F. Cooper. (*See* Cooper, W. F.)

OBITUARY, John Attfield, 144, 155
J. W. Brühl, 84
J. H. van't Hoff, 119
Ocean, atmospheric electricity over, 66
Ogilvie, J. P., determination of sucrose in beet sugar factory products, 21
Oil, cocoanut, in butter and margarine, methods of estimating, 274
Shrewsbury and Knapp's process for estimation, 129
Oils, almond and apricot kernel 189
gas, method for identification, 3, 35
methods of analysis and tests, 148
Oliveri-Mandala, E., and A. Coppola, esterification of isoxazolones with diazomethane, 276
Opium, new alkaloid from, 18
Optical activity, effect of contiguous unsaturated groups on, 68
relation of position isomerism to, 249
relative effects of ethylenic and acetylenic linkings on, 68
Organic amalgams, 231, 257, 268, 280
compounds, action of ultra-violet rays on linear and cyclic, 180
photolysis by ultra-violet rays, 94
progressive phosphorescence at low temperatures, 24
reactivity of halogens in 20, 248

Orientation of nitro-group in nitromyristicinic acid, 78
Orthocarboxyanilides of the sugars, 69
Orthohydroxysulphides, aromatic, and sulphuric acid, interaction, 250
Δ^9-Orthomenthenol(8) and Δ^4-orthomenthenol(8), synthesis of cis- and trans-, 222
Δ^3-Orthomenthenol(8), synthesis, 222
Δ^4-Orthomenthenol(8), synthesis, 222
Orthoveratraldehyde, derivatives, 142
Orton, K. J. P., and Muriel G Edwards. (*See* Edwards, M.G.) and H. King, purification of acetic acid, 249
and H. King, method of chlorination, 285
O'Shea, L. T., "Elementary Chemistry for Coal-mining students" (review), 311
Osmium, chloro-salts of, 84
Osmotic growths, examples of, 293
Ostrogovich, A., action of cyanguanidine on amides, 276
of nitriles on cyanoguanidine, 276
Ostwald, W., "Die Absorption" (review), 130
"Grundriss der Kolloidchemie" (review), 251
Oswald, M., pyrogenation of silver nitrite, 180
Otheoscopes and radiometers, 294
Oxalates, telluric acid, 132
Oxidation in soil, 73, 88
selective, 188
Oxide, uranous, determination of molecular weight of, 251, 312
Oxides, metallic, and phosphoryl chloride, interaction, 297
condensation of ether salts by, 251
Oxyberberine, synthesis, 299
Oxychlorides, mercuric, 288
Oxygen, causes of absorption by lungs of man, 301
determination of amount of dissolved, absorbed by sewage effluents containing nitrites, 274
estimating dissolved, electrochemical method, 154
in air, volumetric determination, 272
separation by cold, 38, 50
Oxyhydroquinone derivatives, 168
Ozone, purification of water by, 38

PAINE, S. G., and A. Harden. (*See* Harden, A.)
Palladium, hydrogenation in presence of, 72
gold alloys, occlusion of hydrogen by, 141
Papaveraldine and xanthaline, identity, 67
Paper, Hughes' reaction of potassium iodide on, and acidity of, 193
Papers, colourless, chemically prepared, 192
Pára rubber, carbohydrate constituents of, 140
Paraöenzoyloxybenzaldehyde, 168
α-parahydroxy-*m*-methoxyethylamine, 115
α-Parahydroxyphenylethylamine, resolution of, 115
β-Paranitrophenol, colour change in, brought about by sunlight, 306
Park, F. E., and L. E. Worthing, rapid method for identification of gas oils, 3
Parkes, A. E., and John D. Roberts, composition of Blaud's pills, 240
pearl coating of pills, 240
Parravano, N., ternary system Ag-Sn-Pb, 275
Parry, W., syntheses of pinacones, 286
Parsons, C. A., and S. S. Cook, experiments on compression of liquids at high pressures, 270
β-Particles variations of ionisation with velocity for, 164
Partington, J. R., cholesterol and fatty acids, 70
determination of dissociation pressures of hydrated salts by a dynamical method, 116
vapour pressures of hydrates by a dynamical method, 70
simple demonstration of Gibbs's phase rule, 70
Pascal, P., magnetic properties of fluorine, 299
utilisation of a magnetic field to determine constitution, 192, 204
Paterson, C. C., and B. P. Dudding, visibility of ships' lights, 273
Peddle, C. J., and W. E. S. Turner, molecular association in water, 68
Pentammineinitrosocobalt salts, sensitiveness to light, 307
Perkin, W. H., jun., experiments on the synthesis of the terpenes, 222
N. Bland, and R. Robinson. (*See* Bland, N.)
and T. Q. Chou. (*See* Chou, T. Q.)
and Bessie Dobson. (*See* Dobson, B.)
W. N. Haworth, and O. Wallach. (*See* Haworth, W. N.)
and E. Hope. (*See* Hope, E.)
and F. R. Lankshear. (*See* Lankshear, F. R.)
and B. D. W. Luff. (*See* Luff, B. D. W.)
W. M. Roberts, and R. Robinson, some derivatives of orthoveratraldehyde, 142
and R. Robinson, synthesis and resolution of gnoscopine, 224
Perman, E. P., chemical action induced by cathode rays and canal rays, 222
direct action of radium on ammonia, 68
Permanganates, absorption spectra in certain solvents, 165
Perrin, J., determination of size of molecules, 312
Petrenko, G. J., and A. S. Fedorow, alloys of silver and cadmium, 312
Petroleum, 3
in turpentine, estimation, 130
Phase difference between primary and secondary currents of a transformer, 80
rule, Gibbs's, 70
Phenanthrene, synthesis, 221
Phenol derivatives containing a mobile nitro-group, syntheses with, 19, 306
Phenols, additive compounds with aromatic polynitro-derivatives, 68
chlorination of, 285
Phenothioxin derivatives, syntheses, 115
Phenylbutine, 204
Phenylhydrazone of camphorquinone, 139
Phenylisoxazolone, azo-derivatives of, 228
Phenylnitromethane, preparation, 132
Philip, A., and L. G. Steele, new form of automatic inflammable gas and vapour detector, 298
and T. Stenhouse, methods of testing inflammable gas and vapour detectors, 298
Philippe, L. H., glucodeconic acids, 24, 95
Phillips, P. F., gum from Bombax malabaricum, 179
Phosphorescence, progressive, at a low temperature, 11
Phosphorescence spectra, progressive, of organic compounds at low temperatures, 24
Phosphorus compounds, experiments to prepare optically active, 275
oxychloride, reduction by hydrogen under action of electric discharge, 23
pentoxide, products obtained by dissolving in water, 101
Phosphoryl chloride and metallic oxides, interaction, 297
Photographic image, relationship between size of particles of silver in gelatin film, and colour of, 143
Photographs, intra-red, 135
of planets, Lowell Observatory, 175
Photolysis of complex acids by ultra-violet rays, 156
of organic compounds by ultra-violet rays, 94
Photomicrography in natural colours, 295
Physical Society, 80, 83, 178, 226, 261, 309
exhibition of apparatus, 9
visit to National Physical Laboratory, 273
Picard, L., and E. E. Blaise. (*See* Blaise, E. E.)
Pickard, R. H., and J. Kenyon, dependence of rotatory power on chemical constitution, 17
Pickering, S. U., cupritartrates and analogous compounds, 68
potassium cupricarbonates, 141
Pickford, P., N. V. Sidgwick, and B. H Wilsdon, (*See* Sidgwick, N. V.)
Pickles, S. S, and B. W. Whitfield, carbohydrate constituents of Pára rubber, 140
Pictet, A., and A. Gams, synthesis of oxyberberine, 299
Picton, T., and R. S. Willows. (*See* Willows, R. S.)
Pierron, P., preparation of aromatic acylguanidines, 95
Pills, Blaud's, composition, 240
pearl coating of, 240
Pinacone, acetylenic, 144
Pinacones, synthesis, 286
Pinene, nitrosoazides of, 78
Pinsker, J., and A Rosenheim. (*See* Rosenheim, A.)
Piotrowski, H., and F. Ephraim. (*See* Ephraim, F.)
Pipes, stream-line motion in curved, 113
Piperidine, imino-derivatives of, leading to formation of ββ-disubstituted glutaric acids, 115
Planets, influence on formation of sun-spots, 164
Lowell Observatory photographs of, 175
Plant extracts, direct guaiacum reaction given by, 259
Plants, distribution of β-glucases in, 17
hydro-electric, in Norway and application to electro-chemical industry, 246
method for estimating gaseous exchanges of submerged, 92
prunase and amygdalase in, 17
water, assimilation in, and its relation to concentration of carbon dioxide, and other factors, 92
Platinum, bromo-salts of, 84
Plimmer, R. H. A., "Practical Physiological Chemistry" (review), 23
Poisons, inorganic, complete destruction of organic matter for detection of, 144
Polynitro-derivatives, aromatic, additive compounds of phenols and phenolic ethers with, 68
Pope, F. G., parabenzoyloxybenzaldehyde, 168
and H. Howard, fluorone derivatives, 140
Pope, W. J., chemical significance of crystal structure, 149, 158
photomicrography in natural colours, 295
Porcelain tubes, gases evolved by walls of, 257
Porter, A. W., and G. Senter. (*See* Senter, G.)
H. L., and W. H. Bragg. (*See* Bragg, W. H.)
Pöschl, V., "Introduction to the Chemistry of Colloids" (review), 34
Potassium and sodium compounds, isomorphism of, 60
metallic, use in determining halogens in benzoyl derivatives, 1
volumetric estimation by cobalti-nitrite method, 282, 291
carbonate, action on magnesium chloride and on solutions of magnesium salts in general, 228
cupricarbonates, 141
ethoxide, 142
fluoride, hydrates of, 299
iodide, Hughes' reaction of, on paper, 193
permanganate, separation of cerium by, 303
persulphate and silver nitrate, 80
Potential, measurement of contact differences of, 311
Pound, J. R. physical properties of mixtures of ether and sulphuric acid, 19
Power, F. B., and C. W. Moore, constituents of bryony-root, 248
and A. H. Salway, constituents of Withania somnifera, 140
Power and its applications, 301
Powney, W. E. F., and J. H. Coste. (*See* Coste, J. H.)
Pratt, L. A., and C. James. (*See* James, C.)
Precipitating, filtering, and drying in an inert gas, apparatus for, 223
Prescott, W. G., and S. Smiles, interaction of aromatic disulphides and sulphuric acid, 165
Pressure, internal, molecular or intrinsic, 247
Pressures, apparatus for maintenance of constant, 165
Preston, H., and E. B. Ludlam. (*See* Ludlam, E. B.)
Price, E. E., chemical significance of crystal structure, 203
Prideaux, E. B. R., second and third dissociation constants of orthophosphoric acid, 249
Priestley, J. H., and F. L. Usher. (*See* Usher, F. L.)
Propiolic compounds, 24
Proteids, transformation into fats during ripening of cheese, 57
Protozoa of soil, 284
Prunase, 17
Pump, mercurial, 9
Purvis, J. E., absorption spectra of chlorobenzene and bromobenzene as vapours, as liquids and in solution, 167
Pyman, F. L., new synthesis of 4(or 5)-β-aminoethylglyoxaline, 215
synthesis of *r*-histidine, 215
and A. J. Ewins. (*See* Ewins, A. J.)
Pyridine, action on iridodisulphates, 23
and copper benzoate, compounds, 222
series, nitrite of base of, 167
Pyrites, sulphur in, determination, 95

QUARTZ, modal illustrating passage of light wave through, 311
Quinaldine synthesis, mechanism of Doebner and von Miller's 115

Quinine and isomerides, absorptian spectra of, 295
estimation as acid citrate in organic liquids, 274
sulphate, radiation, ionisation, and luminescence, 131
Quinol, copper derivative of, 305
course of chemical change in, under influence of radiant energy, 285
Quinoline and copper benzoate, compounds, 222
series, nitrite of base of, 167
Quinone determination by means of titanium chloride, 131
imides, 306

RACE, J., and R. Ross. (*See* Ross, R.)
and F. Maudsley. (*See* Ross, R.)
Radiation effects of secondary X-ray, 179
errors in flow calorimeters, 21
Radiometers and otheoscopes, 294
Radio-telegraphic apparatus, 179
Radium and compounds, chemical properties, 120
direct action on ammonia, 68
emanation, density of, 85, 99
in uranium ores, amount of, 277
radiations, action on some main constituents of normal blood, 284
Raffety, C. W., photographic action of electrical discharges in air at a pressura below that of atmosaphere, 274
Rakshit, J. N., and P. C. Ray. (*See* Ray, P. C.)
Ramsay, Sir W., and R. W. Gray. (*See* Gray, R. W.)
Raschig, F., chemistry of lead chamber process, 81
theory of lead chamber process, 205
Ray, P. C., influence of minute quantities of ferric salts and of manganese nitrate on rate of solution of mercury in nitric acid, 67
and R. L. Datta, nitrates of benzylammonium series, 261
and J. N. Rakshit, methylammonium nitrite, 79
nitrites of alkylammonium bases, 167, 249
and H. K Sen, decomposition of tetramethylammonium nitrite by heat, 67
tetrametnylammonium hyponitrite and its decomposition by heat, 249
Rays, secondary, produced by β-rays, 128
ultra-violet, action on linear and cyclic organic compounds, 180
effects of, 180
nitrification by, 240
Rayner, E. H., three-legged tilting tables with mirrors, 274
Rea, Florence W., C. R. Crymble, A. W. Stewart, and R. Wright. (*See* Crymble, C. R.)
Reaction application o viscometry measurement of rate of, 142
chemical adsorption as preliminary to, 259
Reactions in presence of nickel, 108
Reagents, Grignard, different methods of applying, 114
Reckleben, H., and J. Scheiber. (*See* Scheiber, J.)
Redgrove, H. S., "Alchemy: Ancient and Modern" (review), 240
Reduction, electrolytic, 285
Redwood, Sir B., Turin International Exhibition 1911, 72
Reid, F. S., and M. X. Sullivan. (*See* Sullivan, M. X.)
Reinhardt, C., "Diet and the Maximum Duration of Life" (review), 34
Remfry, F. G. P., acid amides and products of condensation of malonamidea and malonic esters, 167
chemical constitution and hypnotic action, 167
condensation of aromatic aldehydes with nitromethane, 78
Remington, J. S., "Aynsome Annual" (review), 23
Rennie, E. H., and W. T. Cooke, interaction of copper and nitric acid in presence of metallic nitrates, 115
Renoul, Nora, and A. W. Crossley (*See* Crossley, A. W.)
Reverdin, F., and A. de Luc, nitration of mono- and di-acetylated aromatic amines, 24
Reversal, remedy for, 298
Revis, C., and E. R. Bolton (*See* Bolton, E. R.)
Rhead, T. F. E., and R. V. Wheeler, effect of temperature and pressure on equilibrium, $2CO \rightleftharpoons CO_2 + C$, 260
Rhubarb, constituents of, 214
occurrence of alizarin in, 224
Rice, G. S., "Explosibility of Coal Dust" (review), 240
Richards, P. A. E., and C. H. Cribb. (*See* Cribb, C. H.)
Richmond, H. D., composition of milk, 274
River-waters, sulphates in 289
Roberts, E. J., separation of cerium by potassium permanganate, 303
J. D., and A. E. Parkes. (*See* Parkes, A. E.)
W. M., W. H. Perkin, jun., and R. Robinson. (*See* Perkin, W. H., jun.)
Roberts-Austen, Sir W. C., "Introduction to the Study of Metallurgy" (review), 10
Robinson, R., N. Bland, and W. H. Perkin, jun. (*See* Bland, N.)
and E. Hope. (*See* Hope, E.)
W. H. Perkin, jun., and W. M. Roberts. (*See* Perkin, W. H. jun.)
and W. H. Perkin, jun. (*See* Perkin, W. H., jun.)
Roer, E., A. Backe, and A. Wiborg. (*See* Backe, A.)
Roesler, H. A., friction in the bomb calorimeter, 2
Röntgen radiation, energy and distribution of scattered, 66
production and properties of solt, 113
radiations, production of characteristic, 271
Society, 22, 82, 130, 179, 274
Roscoe, Sir, H., and A. Harden, "Inorganic Chemistry for Advanced Students" (review), 143
Rosenhain, W., and S. L. Archbutt, constitution of alloys of aluminium and zinc, 113
and J. C. W. Humfrey, apparatus for making delicate tensile test, 273
Rosenheim, A., and F. Kohn, metatungstic acid, 132
and J. Pinsker, basicity of heter poly acids, 312
and M. Weinheber, gravimetric determination of tellurium and alkalimetric determination of telluric acid, 132
tellur c acid oxalates, 132
Ross, R., and J. P. Leather, rapid method for identification of gas oils, 35
and J. Race, constants of chicken and turkey fats, 189
note on almond and apricot kernel oils, 129
and F. Maudsley, examination of Shrewsbury and Knapp's process for estimation of cocoanut oil, 129
Rost, H., and G. Darzens. (*See* Darzens, G.)
Rotatory power, dependence on chemical constitution, 17
Royal Institution, 13, 56, 71, 72, 89, 112, 120, 127, 155, 160, 192, 212, 228, 252, 300
Photographic Society, 10, 143, 298
Society, 33, 57, 65, 77, 92, 108, 113, 128, 139, 152, 164, 178, 189, 221 239 245, 259, 270, 284, 305
conversazione, 293
presentation of portrait of Sir William Crookes, 92
Rubber mixtures, determination of fillers in, 52
Pára, carbohydrate constituents of, 140
Ruff, O., and H. Goerges, lithium imide, 300
and H. Lickfett, vanadium chlorides, 300
Ruhemann, S., triketohydrindene hydrate, 308
its relation to alloxan, 223
Rule, A., action of hydrogen sulphide on alkyloxides of metals, 142
Ruppin, E., proportion of Cl, SO_3, and σ_0 values in sea-water, 132
Russell, A. S., and W. Marckwald. (*See* Marckwald, W.)
Rust, S., and Helen Chambers. (*See* Chambers, H.)
Rutherford, E., radio-activity of thorium, 22

SABATIER, P., and A. Mailhe, catalytic condenaation of ether salts by metallic oxides, 251
etherification of alcohols by fatty acids, 299
direct etherification by catalysis, 180
and saponification by catalysis, 216
preparation of benzoic ethers, 180
Sabatini, G., and I. Bellucci. (*See* Bellucci, I.)
Sabinene, hydrogenation of, 36
Sackur, O., thermic formation of manganates, 312
Sage, C. E., testing of creosote, 227
Salicylamide and acetyl chloride, condensation, 225
Salmon, E. A., reactions in the electric arc, 36
Salomonson, W., induction coil, 82
Salt solutions, action on iron at various temperatures, 305
Salts, complex, magnetism of, 251
of amine acids, 95
dehydration of, 180
determination of dissociation pressures of, by a dynamical method, 116
hydrated, constancy of water of crystallisation in, 78
metallic, compounds with hexamethylene tetramine, 194
hydrazinates of metallic, 312
influence on autofermentation of yeast, 225
of a green and violet propionatochromium base, 95
of lead fluoride, double, and other halogen salts of lead, 275, 276
of pertitanic acid with organic bases, 191
of rare earths, compounds with hexamethylenetetramine, 275
solubility in corresponding acids, 260
Salter, C. T. C., "Technical Mycology" (review), 34
Salway, A. H., orientation of nitro-group in nitromyristicinic acid, 78
and F. B. Power. (*See* Power, F. B.)
Sand, H. J. S., and R. M. Caven (*See* Caven, R. M.)
and W. M. Smalley, apparatus for rapid electro-analytical determination of metals, 14
glass-frame anode for use with silver and nickel anodes, 14
Sandonnini, C., double salts of lead fluoride and other halogen salts of lead, 275, 276
Sanger-Shepherd, E., remedy for reversal, 298
Sanitation, chemistry of, 278
Saponification by catalysis, 216
Saturn's rings, periodic times of, 241
Scheffer, W., microscopical researches on gelatin film of dry plates, 10
Scheiber, J., and H. Reckleben, constitution of copper acetylide, 191
Schlenk, W., and Anna Herzenstein, triaryl-methyls, 191
Schmeitzner, R., "Clarification of Sewage" (review), 250
Schmidlin, J., and M. Bergman, preparation of ketene from acetone, 130
Schreiner, O., and J. J. Skinner, "Some Effects of a Harmful Organic Soil Constituent" (review), 119
Schuster, A., influence of planets on formation of sun-spots, 164
origin of magnetic storms, 65
periodicity of sun-spots, 66
Schwalbe, C. G., and S. Wolff, studies in carbazole series, 19
Scopeletin, constitution, 248
Scott, A., "Introduction to Chemical Theory" (review), 250
Scott-Hansen, A., hydro-electric plants in Norway, and their application to electro-chemical industry, 246
Scott-Smith, G. E., and J. Evans, analytical and microscopical examination of compound liquorice powder, 189
Sea-water, action on iron at various temperatures, 305
proportion of Cl, SO_3, and σ_0 values in, 132
Sears, J. E., and Dr. Kaye, silica standard metre bar, 273
Seeker, A. F., and W. E. Mathewson, estimation of iodine in organic compounds and separation from other halogens, 61
Sejourné, J., and G. Darzens. (*See* Darzens, G.)
Selenites, anhydrous, 180
Sen, H. K., and P. C. Ray. (*See* Ray, P. C.)
Senderens, J. B., ketones derived from phenylpropionic acid, 180
toluic acids, 120
Senecio alkaloids, action and causation of hepatic cirrhosis in cattle, 305
Senter, G., reactivity of halogens in organic compounds, 20
and A. W. Porter, reactivity of the halogens in organic compounds, 248
Serbin, E., and L. Tchougaeff. (*See* Tchougaeff, L.)
Serum reactions, chemical dynamics of, 178
Sewage effluents containing nitrites, determination of amount of dissolved oxygen absorbed by, 274
Seyewetz, A., and L. Lumière. (*See* Lumière, L.)
Shaw, P. E., measurement of end-standards of length, 34
W. B., salts of dinitrodihydroxybenzenes, 71
3:5-dinitroquinol, 223
Sheod, O. M., volumetric determination of potassium by the cobalti-nitrite method, 282, 291
Sheets, Guinnevere, fruit of Cornus paniculatum, 172

Ship lights, visibility of, 273
models, apparatus for moulding and shaping, 273
Shrewsbury, H. S., estimation of petroleum in turpentine, 130
and Knapp's process for estimation of cocoanut oil, 129
Shrivell, F. W. E., and B. Dyer. (*See* Dyer, B.)
Sidgwick, N. V., "Organic Chemistry of Nitrogen" (review), 59
P. Pickford, and B. H. Wilsdon, solubility of aniline in aqueous solutions of its hydrochloride, 261
and B. H. Wilsdon, conductivity and viscosity of aqueous solutions of aniline hydrochloride at 25°, 261
Silica standard metre bar, 273
tubes, gases evolved by walls of, 257
Silicates, thermo-chemistry of, 132
Silicoethane and silicoethylene derivativea, 287
Silicole, tertiary, preparation, 69
Silicon, brominated and hydrobrominated compounds of, 36
organic derivatives of, 69
chlorobromides and chloroiodides, 228
Silver and cadmium alloys, 312
and tin, amalgams containing, 67
chloride and bromide, differentiation of latent images obtained with emulsions of, 252
reduction, 288
nitrate and potassium persulphate, interaction, 80
interaction of esters of bromo-substituted fatty acids with, in alcoholic solutions, 20
nitrite, pyrogenation, 180
Simpson, G. C., and C. S. Wright, atmospheric electricity over the ocean, 66
Sjöstedt, P., and F. Fichter. (*See* Fichter, F.)
Skinner, J. J., and O. Schreiner. (*See* Schreiner, O.)
Smalley, W. H., and H. J. S. Sand. (*See* Sand, H. J. S.)
Smelting of materials containing lead, 275
Smiles, S., syntheses of thioxanthone and derivatives, 19
and T. P. Hilditch. (*See* Hilditch, T. P.)
and W. G. Prescott. (*See* Prescott, W. G.)
Smith, A. M., and F. F. Blackman. (*See* Blackman, F. F.)
F. E., Lorenz apparatus, 273
S. W. J., and W. F. Higgins, surface effects between mercury and certain solutions, and electrochemical method of estimating dissolved oxygen, 154
W., ammonium sulphate and its instability, 116
hydrolysis of ammonium salts, 116
Smoke utilisation and prevention, 288
Soaps in solution, constitution, 68
Society of Chemical Industry (London Section), 21, 81, 116, 129, 179, 227, 297
of Public Analysts, 12, 129, 189, 239 274
Soda crystals, efflorescence of washing, 45
Soddy, F., chemistry of mesothorium, 17
Sodium amalgams, physico-chemical study of, 181, 198, 207
and potassium compounds, isomorphism of, 60
vapour, ammonium dispersion, 9
azide and nitrosates, interaction, 78
ethoxide, 142
hydrogen carbonate, 295
Sodium hypophosphite, action on copper sulphate in aqueous solution 236
ketones, action of chlorocarbonic ether on, 228
stearate in solutions, electrical conductivity, 68
thiosulphate, action of hypoiodites on, 130
Sofianopoulos, A. I., two new compounds of stannous chloride and ammonia, 263
Soil, oxidation in, 73, 88
protozoa of, 284
Solder, determination of tin and antimony in, 147
Solids, molecular volumes of, 144
Solubility coefficients, determination by aspiration, 79
Solute in solution, volume of, 222
Solution, bearing of solvate theory of, 125
Solutions, processes operative in, 97, 109, 121, 133, 145, 168
Sommerfeldt, E., isomorphism of potassium and sodium compounds, 60
Spark, electric, formation of dust striations by, 226
trains, 273
Specific inductive capacity, measurement of, 128
Spectra, absorption, of benzene derivatives, 116
of chlorobenzene and bromobenzene as vapours, as liquids, and in solution, 167
of chlorobenzene, the dichlorobenzenes, and chlorotoluenes, 167
of cinchonine, quinine, and their isomerides, 295
of lithium and cæsium, 152
of metallic ions and their valency, relation between, 166
of permanganates in certain solvents, 165
progressive phosphorescence, of organic compounds at low temperatures, 24
vacuum tube, of mercury, 271
Spectrum of nitrogen afterglow, 294
photographs showing composition of tails of comets, 294
Sperry, E. A., power and its applications, 301
E. S., fluxes as applied to brass foundry, 31
Spices used in veterinary medicines, evaluation of, 240
Spitalsky, E., catalysis by chromic acid and its salts, 96
Stannous chloride and ammonia, compounds of, 263
Starch purification, 12
Steam, action on iron at high temperatures, 250
Steel, Lüders' lines on mild, 300
Steele, L. G., and A. Philip. (*See* Philip, A.)
Stennouse, T., and A. Philip. (*See* Philip, A.)
Stephenson, H. H., molecular volumes of solids, 144
"Who's Who in Science," 300
Stevens, H. P., and C. Beadle. (*See* Beadle, C.)
Stewart A. W., C. R. Crymble, R. Wright, and W. G. Glendinning. (*See* Crymble, C. R.)
C. R. Crymble, R. Wright, and Florence W. Rea. (*See* Crymble, C. R.)
Stilbenediol diacetates, nitration, 115
Stimulants, action in promoting enzymic activity, 293
Stoddard, J. T., "Introduction to General Chemistry" (review), 119
Stoermer, R., conversion of stable isomers into labile form by ultra-violet light, 264
Stovaine and homologues, physical and physiological properties, 92
Strachan, J., Hughes' reaction of potassium iodide on paper, 193
note on catalytic action of copper oxide, 241
Stream line motion in curved pipes, 113
Stream-lines past an elliptic cylinder, diagrams of, 261
Strong, W. W., report on chemical constitution and the absorption of light, 46, 55, 64, 75 90
and H. C. Jones (*See* Jones, H. C.)
Strontium and calcium, separating and identifying, sulphite method, 157
preparation of crystallised, 12
Strutt, R. J., chemically-active modification of nitrogen produced by electric discharge 183, 221
and A. Fowler. (*See* Fowler, A.)
Strychnine and cocaine, and atropine, separation and determination, 185
Sublimation apparatus, 138
Sucrose in beet sugar factory products, determination by Clerget's process, 21
Sudborough, J. J., and S. H. Beard, additive compounds of phenols and phenolic ethers with aromatic polynitro-derivatives, 63
Sugars, influence of arsenates and arsenites on fermentation of by yeast-juice, 139
orthocarboxyanilides of, 69
Sullivan, M. X., and F. R. Reid, oxidation in soil, 73 88
Sulphanilide, 84
Sulphates, determining, 191
double, formed by sulphates of lanthanum and cerium with alkaline sulphates, 23
in river-waters, 289
Sulphides, aromatic, electrolytic oxidation, 131
Sulphite method for separating and identifying strontium and calcium, 157
Sulphohydrazide, 300
Sulphur and compounds, action on hydrazine, 300
compounds, new series of aromatic, 312
in pyrites and marcasite, determination, 95
dioxide, action on ammonia, 300
Sun-spots, influence of planets on formation, 164
periodicity of, 66
Sutherland, Brenda, and Leila Green. (*See* Green, L.)
W. G., "Dispensing Made Easy" (review), 130
Suzuki, T., change of cobaltous into cobaltic nitrite, 104
Swinburne, J., separation of oxygen by cold, 38, 50
Swinton, A. A. Campbell, a 10,000 volt storage battery, 130
Syson, phenomena of regeneration in, and structure of its collar-cells, 239
Symes, W. L., and V. H. Veley, certain physical and physiological properties of atovatue and its homologues, 92
effect of some local anæsthetics on nerve, 92
Syntheses with phenol derivatives containing a mobile nitro-group, 19, 306

TABLES of constants and numerical data, 204
three-legged tilting, with mirrors, 274
Tarbouriech, E., and M. Godchot. (*See* Godchot, M.)
Tantalum and columotium, separating, 103
determining, indirect method, 52
Tautomerism, experiments on, 249
Taylor, H. S., and H. Bassett, jun. (*See* Bassett, H., jun.)
W. E., precipitation of aluminium hydroxide in the granular form, 169
Tchougaeff, L., and W. Fomin, hydrogenation of isomeric thujenes and of sabinene 36
and E. Serbin, complex salts of some amino acids, 95
Tellurium and cadmium alloys, 60
and tin alloys, 60
determination, gravimetric, 132
gold, metallography of the system, 263
Temperature scale between 100° and 500° C., 25
vertical, distribution in atmosphere over England, 245
Temperatures, high, general discussion on, 240
measurement of, 179
Tension, measurement of surface, 155
Ternary system, Ag-Sn-Pb, 275
Terpenes, synthesis of, 141, 142, 222
Terpineol, nitrosoazides of, 78
Tetramethyl ammonium amalgam, properties of, 257
Tetramethylammonium hyponitrite and its decomposition by heat, 249
nitrite, decomposition by heat, 67
Tetranitromethane, 12
Thermo-regulator, electric, 262
sensitive, 178
Thiobenzanilide, action of hydrogen dioxide on, 248
preparation, 63
Thiophenic compound, $C_{16}H_8S_2$, and derivatives, 120
Thioxanthone and derivatives, syntheses of, 19
Thole, F. B., and J. F. Thorpe, experiments on tautomerism, 249
formation and reactions of imino-compounds, 115
Thomas, F., and I. S. Cardell. (*See* Cardell, I. S.)
Thomlinson, J. C., celluloid in a dangerous form 12
estimation of free ammonia and ammonium carbonate by titration, 13
Thompson, H. V., copper derivative of quinol, 305
S. P., new method of harmonic analysis by averaging selected ordinates, 310
subjective nature of difference tone, 310
and E. G. Coker, experiments with polarised light, 293
Sir J. J., method of chemical analysis, 265
Thomson displacement apparatus for manufacture of gun cotton, composition of acids flowing from, 116
Thorium, radio-activity of, 22
Thorp diffraction gratings, 9
Thorpe, J. F., note on preparation of β-hydrindone 261
and F. B. Thole. (*See* Thole, F. B.)
Thujenes, hydrogenation of isomeric, 36
Tian, A., decomposition of hydrogen peroxide by light, 36
water by ultra violet light, 281
Tin and silver, amalgams containing, 67
and tellurium alloys, 60
dross, reduction in an electric furnace, 33
in soft solder, determination, 147
ores, decomposing, 143
Tantalum and columotium, separating, 103
determining, indirect method, 52
Tautomerism, experiments on, 249
Taylor, H. S., and H. Bassett, jun. (*See* Bassett, H., jun.)
W. E., precipitation of aluminium hydroxide in the granular form, 169
Tchougaeff, L., and W. Fomin, hydrogenation of isomeric thujenes and of sabinene 36
and E. Serbin, complex salts of some amino acids, 95
Tellurium and cadmium alloys, 60
and tin alloys, 60
determination, gravimetric, 132
gold, metallography of the system, 263
Temperature scale between 100° and 500° C., 25
vertical, distribution in atmosphere over England, 245
Temperatures, high, general discussion on, 240
measurement of, 179
Tension, measurement of surface, 155
Ternary system, Ag-Sn-Pb, 275
Terpenes, synthesis of, 141, 142, 222
Terpineol, nitrosoazides of, 78
Tetramethyl ammonium amalgam, properties of, 257
Tetramethylammonium hyponitrite and its decomposition by heat, 249
nitrite, decomposition by heat, 67
Tetranitromethane, 12
Thermo-regulator, electric, 262
sensitive, 178
Thiobenzanilide, action of hydrogen dioxide on, 248
preparation, 63
Thiophenic compound, $C_{16}H_8S_2$, and derivatives, 120
Thioxanthone and derivatives, syntheses of, 19
Thole, F. B., and J. F. Thorpe, experiments on tautomerism, 249
formation and reactions of imino-compounds, 115
Thomas, F., and I. S. Cardell. (*See* Cardell, I. S.)
Thomlinson, J. C., celluloid in a dangerous form 12
estimation of free ammonia and ammonium carbonate by titration, 13
Thompson, H. V., copper derivative of quinol, 305
S. P., new method of harmonic analysis by averaging selected ordinates, 310
subjective nature of difference tone, 310
and E. G. Coker, experiments with polarised light, 293
Sir J. J., method of chemical analysis, 265
Thomson displacement apparatus for manufacture of gun cotton, composition of acids flowing from, 116
Thorium, radio-activity of, 22
Thorp diffraction gratings, 9
Thorpe, J. F., note on preparation of β-hydrindone 261
and F. B. Thole. (*See* Thole, F. B.)
Thujenes, hydrogenation of isomeric, 36
Tian, A., decomposition of hydrogen peroxide by light, 36
water by ultra violet light, 281
Tin and silver, amalgams containing, 67
and tellurium alloys, 60
dross, reduction in an electric furnace, 33
in soft solder, determination, 147
ores, decomposing, 143

Tinkler, C. K., constitution of berberine, 307
Titanium chloride, determination of quinone by means of, 131
Titherley, A. W., and W. L. Hicks, condensation of acetyl chloride and salicylamide, 225
and E. C. Hughes, 6-bromo-2-phenyldihydro-1:3-benzoxazine-4-one and related derivatives, 20
Tone, subjective nature of difference, 310
Tops, spinning, 310
Townsend, J. S., charges on ions in gases and some effects that influence the motion of negative ions, 33
Transformer, demonstration of phase difference between primary and secondary currents of, 80
Traube's molecular volume method applied to binary mixtures of organic substances, 18
Trialkylammonium nitrite, 167
Triarylmethyls, 191
β-Triazoethylamine, 297
Triazo-group, 78, 297
Triketohydrindene hydrate, 308
relation to alloxan, 223
Trimethylammonium nitrite, 167, 249
Trimethylcarbinol, cryoscopic, ebullioscopic and association constants of, 20
1:1:2-Trimethylcyclohexan-3-one, 285
Tronson, C. A., F. C. Frary, and H. R. Bicknell. (*See* Frary, F. C.
Troup, E., smelting of metals containing lead, 275
Trouton, F. T., demonstration of phase difference between the primary and secondary currents of a transformer, 80
Trypanosoma gambiense, experiments to ascertain if antelope may act as reservoir of virus of, 57
domestic fowl of Uganda may act as reservoir of virus of, 58
Trypanosomiasis, autoagglutination of red blood cells in, 57
Tryptopham, formation of 3-β-aminoethylindole from, 20
Tswett, M., crystallised chlorophyll, 51
Turin, International Exhibition, 1911, 72
Turkey fat, constants for, 189
Turner, Emily G., and J. Kenner. (*See* Kenner J.)
T., "Lectures on Iron Foundring" (review), 287
W. E. S., molecular association and its relationship to electrolytic dissociation, 114
and C. J. Peddle. (*See* Peddle, C. J.)
Turpentine, petroleum in, estimation, 130
substitutes, 190
Tutin, F., constituents of bulb of Buphane disticha, 295
and H. W. B. Clewer, constituents of rhubarb, 214
Tutton, A. E. H., "Crystallography and Practical Crystal Measurement" (review), 215
Tyrer, D., method for accurate estimation of traces of water in ether, 286
volume of a solute in solution, 222

UGANDA, experiments to ascertain if domestic fowl of, may act as reservoir of virus in sleeping sickness, 58
Umney, J. C., and C. T. Bennett, evaluation of certain spices used in veterinary medicines, 240
Uranium ores, amount of radium contained in, 277
volumetric determination, 146
carbide, formula of, 208
Uranyl salts, duration of phosphorescence, 216
nitrate and its ethereal solution, 191
Urbain, G., new element accompanying lutecium and scandium in earths of gadolinite, celtium, 73
Usher, F. L., and J. H. Priestley, mechanism of carbon assimilation, 284

VALENCY numbers and molecular volumes, relation between, 263
Valeur, A., and C. Moureu. (*See* Moureu, C.)
Van Bemmelen, J. M., "Die Absorption" (review), 130
Van Gelderen, F. M., and M. O. Forster. (*See* Forster, M. O.)
Van Klooster, H. S., behaviour of metaboric and metaphosphoric acids in the melts of their alkali salts, 95
binary systems, 95
Van 't Hoff, J. H., obituary, 119
Vanadium chlorides, 300
Vanstone, E., physico-chemical study of mercury sodium alloys or sodium amalgams, 181, 198, 207
Vapour and gas detector, automatic inflammable, 298
detectors, testing inflammable, 298
pressures, optical method of measuring, 270
Vegetable assimilation and respiration, 92
products, determining ash in, 252
Veley, V. H., reactions between chemical compounds and living muscle proteins, 67
and W. L. Symes. (*See* Symes, W. L.)
Veterinary medicines, evaluation of spices used in, 240
Viburnum lentago, fruit of, 205
Vicianose and vicinine, constitution, 24
Vignon, L., action of water-vapour on carbon in presence of lime, 263
Viguier, P. L., α-bromcrotonic aldehyde, 156
Villavecchia, V., "Dizionario di Merceologia e di Chimica Applicata" (review), 94
Viscometry, application to measurement of rate of reaction, 142
Viscosity, correlation with other constitutive properties, 19
with other physical properties, 222
Volume of a solute in solution, 222
Vournasos, A. G., some well-defined bismuthides, 252

WADE, J., and R. W. Merriman, apparatus for maintenance of constant pressures, 165
influence of water on boiling-point of ethyl alcohol, 165
Wahl, A., condensation of acetic ether with its higher homologues, 120
W. A., chemistry of meteorites, 60
Waidner, C. W., and G. K. Burgess, note on the temperature scale between 100° and 500° C., 25
Walden, A. E., and G. D. Lander. (*See* Lander, G. D.)
Walker, A. J., and O. E. Mott, "Text-book of Organic Chemistry" (review), 227
E. W. A., variation and adaptation in bacteria, 178
J., "Introduction to Physical Chemistry" (review), 118
Maggie, and H. Crompton. (*See* Crompton, H.)
Wallach, O., W. N. Haworth, and W. H. Perkin, jun. (*See* Haworth, W. N.)
Walpole, G. S., action of B. lactis aerogenes on glucose and mannitol, 57
Walsh, Gertrude M., V. J. Harding, and C. Weizmann. (*See* Weizmann, C.)
Warwick, F. J., "Dispensing Made Easy" (review), 130
Water, decomposition by ultra-violet light, 281
ethyl alcohol, acetic acid, and ethyl acetate, equilibrium in system, 287
in ether, estimation of traces, 286
molecular association in, 68
motion of oscillating, 66
of crystallisation in hydrated salts, constancy of, 78
purification by ozone, 38
softening, time, temperature, and composition as factors in, 62
specific heat of, 128
temperature of action of alkali metals on, 263
vapour, action on carbon in presence of lime, 263
Waters, occurrence of penta-thionic acid in natural, 69
Watson, E. R., aminoquercetin, 308
H. E., method for accurate volumetric determination of oxygen in air, 272
Wattmeter, high-tension electrostatic, 226
Waves, electrical, occurring in nature, 153
Weinheber, M., and A. Rosenheim. (*See* Rosenheim, A.)
Weinland, R. F., and K. Hoehn, salts of a green and a violet propionato-chromium base, 95
Weintraub, E., cast copper of high electrical conductivity, 187
Weir, J., new derivatives of aminolauronic acid, 297
Weiss, P., rationality of ratios of magnetic moments of atoms, and a new universal constituent of matter, 137
Weisweiller, G., and G. Bertrand. (*See* Bertrand, G.)
Weizmann, C., and R. Alpern. (*See* Alpern, R.)
V. J. Harding, and Gertrude M. Walsh. (*See* Harding, V. J.)
and A. Hopwood. (*See* Hopwood, A.)
Werner, A., "New Ideas on Inorganic Chemistry" (review), 215
Westcott, W. W., and W. H. Martindale. (*See* Martindale, W. H.)
Wheeler, E., and H. E. Armstrong. (*See* Armstrong, H. E.)
R. V., and M. J. Burgess. (*See* Burgess, M. J.)
and T. F. E. Rhead. (*See* Rhead, T. F. E.)
Wheldale, Miss M., direct guaiacum reaction given by plant extracts, 259
Whiddington, R., production and properties of soft Röntgen radiation, 113
of characteristic Röntgen radiations, 271
White, E., "Analytical Reagents, Standards and Tests" (review), 250
Whitfield, B. W., and S. S. Pickles. (*See* Pickles, S. S.)
Whittaker, E. T., dynamical value of the molecular systems which emit spectra of the banded type, 189, 221
Wiborg, A., A. Backe, and E. Roer. (*See* Backe, A.)
Wiesbaden, Chemical Laboratory Fresenius, 132
Wigdorow, S., and G. Jantsch. (*See* Jantsch, G.)
Wilde, H., periodic times of Saturn's rings, 241
Wile, R. S., reduction of tin dross in an electric furnace, 33
Wiley, H. W., "U.S. Department of Agriculture, Report of Chemist for 1910" (review), 311
Willows, R. S., and T. Picton, behaviour of incandescent lime cathodes, 226
Wilsdon, B. H., and N. V. Sidgwick. (*See* Sidgwick, N. V.)
and P. Pickford. (*See* Sidgwick, N. V.)
Wilson, Prof., spark coil apparatus, 9
C. T. R., method of making visible the paths of ionising particles through a gas, 245
E., high-tension electrostatic Wattmeter, 226
W., variation of ionisation with velocity for β-particles, 164
Wires, experimental measurement of high-frequency resistance of, 80
Withania Somnifera, constituents of, 140
Wohl, A., and F. Koch, sulphanilide, 84
Wolff, S., and C. G., Schwalbe. (*See* Schwalbe, C. G.)
Wood, T. B., "Course of Practical Work in Agricultural Chemistry" (review), 299
Wootton, W. O., and W. H. Hurtley (*See* Hurtley, W. H.)
Worley, F. P., and H. E. Armstrong. (*See* Armstrong, H. E.)
Worthing, L. E., and F. E. Park. (*See* Park, F. E.)
Wright, C. S., and G. C. Simpson. (*See* Simpson, G. C.)
R., sublimation apparatus, 138
C. R. Crymble, A. W. Stewart, and W. G. Glendinning. (*See* Crymble, C. R.)
and Florence W. Rea. (*See* Crymble, C. R.)

X-RAY tube, 9
X-rays, action on developing chick, 57
energy transformations of, 270
Xanthaline and papaveraldine, identity of, 67
Xanthates, metallic, decomposition by heat, 263

YEAST, autofermentation, influedce of salts on, 225
juice, alcoholic ferment of, 139
Yorke, W., autoagglutination of red blood cells in trypanosomiasis, 57

Young, W. J., and A. Harden. (*See* Harden, A.)
Yttrium nitrate, basic, 42

ZERR, G., "Tests for Coal-tar Colours in Aniline Lakes" (review), 93
Zimmerli, A., and M. O. Forster. (*See* Forster, M. O.)
Zinc, action of chlorides of α-alkoxyl acids on organo-metallic compounds of, 156, 191
Zinc and aluminium alloys, constitution, 113
determination from citric acid solutions, 15
in ores, electrolytic determination of, 174
Zinc chromates, 312
Zincke, T., new series of aromatic sulphur compounds, 312

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